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CALCULATIONS OF QUANTITATIVE CHEMICAL ANALYSIS

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CALCULATIONS OF QUANTITATIVE CHEMICAL ANALYSIS

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PREFACE TO THE SECOND EDITION

In preparing the second edition of this text, the general arrangement of the first edition has been followed. Several additions and changes have, however, been made. Chapters and problems on electrometric titrations and on equilibrium constants have been inserted. The descriptive matter has been expanded in several instances, especially in the sections devoted to precision measures, calibration of weights, electrolysis, and indicators. Many problems and illustrative examples have been added and the miscellaneous problems have been rearranged and classified under descriptive headings.

L. F. H.
S. G. S.

Cambridge, Mass.
December, 1926.

PREFACE TO THE FIRST EDITION

Instruction in Quantitative Chemical Analysis is usually divided between laboratory exercises and class-room lectures or recitations. The laboratory exercises serve to illustrate the various chemical principles which are discussed in the class-room, and to give opportunity for acquiring manipulative skill in the use of chemical apparatus. Quantitative Analysis is a very practical branch of chemistry, however, and a knowledge of the chemical principles involved and the acquirement of manipulative skill are of little practical value unless they are accompanied by an ability to compute and interpret results from analytical data, and to do this quickly and correctly. Consequently, in a well balanced course of instruction it is necessary to devote a portion of the time to stoichiometric principles and to the solution of practical and illustrative problems. To decide just how much time should be devoted to this phase of the subject is often a matter of considerable difficulty, especially when the time available for the course is limited. It has usually been necessary to choose between two procedures,—either to include the stoichiometric discussions in the class-room work, or to allow the student to shift for himself and make the necessary calculations by any methods he may devise.

The authors believe that class-room work in Quantitative Analysis should be devoted primarily to the discussion of chemical principles and that too extensive discussion of mathematical computations must seriously encroach upon time which may be devoted to more essential topics. On the other hand, when left to himself, the student evolves methods of computation which are often inaccurate and almost always laborious and time-consuming.

It is with the view of solving these difficulties that this volume has been prepared. It attempts to attain the following objects: (1) to allow the instructor to devote more time in the class-room to the chemistry of Quantitative Analysis; (2) to aid the

student in grasping stoichiometric principles without extensive personal instruction; (3) to provide ample material for home assignments and quizzes; (4) to prepare the way to more difficult problem work in Physical Chemistry and Chemical Engineering.

In preparing this book, the material has been divided into numerous short chapters. Each chapter contains groups of problems similar to those discussed in the corresponding text, and finally, a large number of miscellaneous problems are given several of which are taken from past examination papers at the Massachusetts Institute of Technology. Altogether, about six hundred problems are included, all of which may be solved by simple arithmetic or algebra. An attempt has been made to cover nearly all the common analytical procedures and to furnish enough material to allow considerable variation in assignments from year to year. Although the problems are devoted primarily to Quantitative Analysis, other phases of chemical work are purposely included in order that the student may have opportunity to apply the knowledge which he has already acquired from his previous courses. The question of the advisability of including answers has been given some attention. In the case of problems used for purposes of self-instruction, the inclusion of answers is highly advisable, but in the case of problems assigned for home work and especially for quizzes, it is oftentimes desirable that the answers be omitted. In view of the fact that a large number of problems are given, it has been thought best to effect a compromise and include answers to about one-half of the problems.

The authors wish to acknowledge their indebtedness to Professor R. S. Williams whose suggestions and advice have been invaluable. Thanks are also due M. M. Green and C. E. Carlson for assistance in reading the proof and for other services.

The authors will welcome any corrections of mathematical or typographical errors which may be called to their attention.

L. F. H.
S. G. S.

CAMBRIDGE, MASS.,
May, 1922.

CONTENTS

PART I

General and Gravimetric Analysis

CHAPTER I

Computation Rules of Quantitative Analysis

		Page
1.	Factors Influencing the Reliability of Analytical Results	1
2.	Deviation Measures as a Means of Expressing Reliability	2
3.	Significant Figures as a Means of Expressing Reliability	3
4.	Rules Governing the Use of Significant Figures in Chemical Computations	3
5.	Solution of Numerical Problems	6
	Problems	7

CHAPTER II

Chemical Equations

6.	Purpose of Chemical Equations	9
7.	Writing and Balancing Equations	9
	Problems	14

CHAPTER III

The Chemical Balance

8.	Sensitiveness of the Chemical Balance	16
9.	Conversion of Weight in Air to Weight in Vacuo	16
10.	Calibration of Balance Weights	10
	Problems	21

CHAPTER IV

Equilibrium Constants

11.	Law of Mass Action	23
12.	Ionization Constant	23
13.	Polybasic Acids	25
14.	Solubility Product	26
	Problems	27

CHAPTER V

Calculations of Gravimetric Analysis

15.	The Law of Definite Proportions Applied to Calculations of Gravimetric Analysis	29

PAGE
16. Calculations from Equations 29
17. Chemical Factors 31
Problems 33
18. Application of Chemical Factors to Percentage Computations . . 34
Problems 35
19. Gravimetric Problems Involving a Factor Weight Sample 36
Problems 38
20. Calculation of the Volume of a Reagent Required for a Given Reaction 39
Problems 42
21. Indirect Analyses 43
Problems 45
22. Calculation of Atomic Weights 46
Problems 49
23. Analysis by Electrolysis 51
Problems 55

CHAPTER VI

CALCULATIONS FROM REPORTED PERCENTAGES

24. Calculations Involving the Elimination or Introduction of a Constituent 59
Problems 61
25. Calculation of Molecular Formulae from Chemical Analyses . . . 63
26. Calculation of Formulae of Minerals Exhibiting Isomorphic Replacement 65
Problems 67

PART II

Volumetric Analysis

CHAPTER VII

CALIBRATION OF MEASURING INSTRUMENTS

27. Measuring Instruments in Volumetric Analysis 71
28. Calculation of the True Liter 71
29. Calculation of the Mohr Liter 73
Problems 74

CHAPTER VIII

CONCENTRATION OF SOLUTIONS

30. Standard Solutions 76
31. Unit Weight per Unit Volume 76
32. Percentage Composition 76
33. Molal Concentration 77
34. Normal Concentration 78
35. Divisions of Volumetric Analysis 79

CHAPTER IX

Acidimetry and Alkalimetry

Page

36. Equivalent Weights Applied to Acidimetry and Alkalimetry . . . 80
Problems . . . 81
37. Ratio of Reacting Solutions . . . 83
Problems . . . 83
38. Adjusting Solutions to a Desired Normality . . . 84
Problems . . . 85
39. Normality of a Solution Made by Mixing Similar Constituents . . 86
Problems . . . 86
40. Determination of the Normality of a Solution from Its Quantitative Preparation . . . 87
41. Determination of the Normality of a Solution by Titration against a Solution of Known Concentration . . . 88
42. Determination of the Normality of a Solution by Titration against a Substance of Known Purity . . . 89
Problems . . . 90
43. Calculation of Percentage Purity from Titration Values . . . 91
Problems . . . 94
44. Problems in Which the Volume of Titrating Solution Bears a Given Relation to the Percentage of Constituent Present . . . 96
Problems . . . 97
45. Determination of Proportion in Which Components are Present in a Pure Mixture . . . 98
Problems . . . 99
46. Effect of the Sensitiveness of an Indicator on an Acidimetric Titration . . . 100
Problems . . . 103
47. Relation of the Equivalent Weight of an Acid or Base to the Indicator Used . . . 103
48. Calculation of Analyses Involving the Use of Two Indicators . . 104
Problems . . . 110
49. Double Indicator Problems Applied to Titrations with Mixed Alkali Solutions . . . 112
Problems . . . 114
50. Titration of Acid Mixtures . . . 115
51. Special Cases of Acid Mixtures . . . 116
Problems . . . 118

CHAPTER X

Oxidation and Reduction Methods

52. Fundamental Principles . . . 119
53. Equivalent Weights of Oxidizing and Reducing Agents . . . 119
54. Calculations of Oxidation and Reduction Processes . . . 129
Problems . . . 135

CHAPTER XI

Saturation or Precipitation Methods

Page
55. Calculations Involved 142
Problems 144

PART III

Gas Analysis

CHAPTER XII

Calculations of Gas Analysis

56. Fundamental Laws 147
57. Gas Volumetric Methods 149
58. Correction for Water Vapor 150
59. Calculations of Gas Volumetric Analysis 151
Problems 151
60 Absorption Methods 154
61. Combustion Methods 155
Problems 159

PART IV

Potentiometric Analysis

CHAPTER XIII

Electrometric Titrations

62. Electromotive Series 163
63. Nernst Formula 165
64. Application of Nernst Formula to Electrometric Titrations. . . . 167
65. P_H Value 168
66. Electrometric Titration Apparatus 169
67. Oxidation and Reduction Titrations. 170
Problems 172

PART V

Miscellaneous Problems

Significant Figures, Precision Measures, Chemical Balance. 173
Ionization Constants, Solubility Products 175
Chemical Factors, Atomic Weights 177
Volumes of Reagents 179
Indirect Gravimetric Analyses 179
Electrolysis 181
Elimination of a Constituent, Empirical Formulae 182
Calibration of Measuring Instruments. 186
General Acidimetry. 187
Indicators 191

PAGE
Double Indicator Problems, Oleum Analysis 192
General Oxidation Methods 194
Permanganate Process, Dichromate Process, Iodimetry 195
Electromotive Series, Electrometric Titrations 198
Precipitation Methods 200
Gas Analysis 201
Halides, Silver, Alkalies 202
Alkaline Earths, Limestone 203
Aluminum, Iron, Cobalt, Nickel 205
Copper, Zinc, Lead, Tin, Non-ferrous Alloys 206
Nitrogen, Phosphorus, Vanadium, Arsenic, Antimony 208
Hydrogen, Oxygen, Sulphur 211
Carbon, Silicon, Titanium, Tungsten 212
Manganese, Chromium 214
General and Miscellaneous Analyses 216

APPENDIX 219

INDEX 237

CALCULATIONS OF QUANTITATIVE CHEMICAL ANALYSIS

PART I

GENERAL AND GRAVIMETRIC ANALYSIS

CHAPTER I

COMPUTATION RULES OF QUANTITATIVE ANALYSIS

1. Factors Influencing the Reliability of Analytical Results.—Quantitative Chemical Analysis deals with the methods of determining the proportions in which constituents and components are present in given compounds or mixtures. For convenience, the subject is divided into three parts—Gravimetric Analysis, Volumetric Analysis, and Gas Analysis, and all methods involve the careful measurement of masses and volumes of chemical substances. From the numerical data obtained from these measurements the desired proportions may be calculated. It is found, however, that duplicate analyses of the same substance, even when made by experienced analysts following identical methods, rarely give numerical values which are exactly the same. Furthermore, the discrepancy between results is found to depend upon the method used, and an analytical result obtained by one procedure may differ from a similar result obtained by an entirely different procedure. The most important factors which thus influence the precision of analytical results are probably the following: (1) the manipulative skill of the analyst; (2) the experimental errors of the procedure itself, such as the slight solubility of substances assumed to be insoluble or the contamination of precipitates assumed to be pure; (3) the accuracy of the measuring instruments used; and (4) sudden fluctuations of temperature and barometric pressure. In

order, therefore, that a numerical result obtained from chemical measurements may be of scientific or technical value, the result must be accompanied by data which will give to an observer at least a general idea of its reliability.

2. Deviation Measures as a Means of Expressing Reliability. In general, the precision of a numerical result is best expressed by means of so-called "deviation measures" and "precision measures" such as are often used in accurate physical measurements. Thus, repeated independent readings of a burette gave the following values:

(*a*) 43.74
(*b*) 43.76
(*c*) 43.76
(*d*) 43.75
(*e*) 43.77
(*f*) 43.75
(*g*) 43.75
(*h*) 43.76
(*i*) 43.73
Mean = 43.753

The most probable value for this reading is obviously the *mean*, 43.753, which is obtained by dividing the sum of the readings by the number of readings taken. The *deviation* of each measurement from this mean, regardless of sign, is shown in the following:

(*a*) 0.013
(*b*) 0.007
(*c*) 0.007
(*d*) 0.003
(*e*) 0.017
(*f*) 0.003
(*g*) 0.003
(*h*) 0.007
(*i*) 0.023
Mean deviation = 0.0092

The *mean deviation*, 0.0092, represents the amount by which an average single independent reading differs from the most probable value, and is therefore a measure of the reliability of a

single observation. It is more important, however, to know the reliability of the mean than that of a single observation. It can be shown that the reliability of a mean or average value is numerically equal to the average deviation of a single observation divided by the square root of the number of observations taken. In the above the *average deviation of the mean* is $\frac{0.0092}{\sqrt{9}} = 0.0031$, and the value for the reading may be expressed as 43.753 ± 0.0031. (It is customary to use only two significant figures in all deviation measures.) When several such measurements are involved in a computation it is possible to calculate from the deviation measure of each measurement the deviation measure or precision measure of the final result, and thus obtain a numerical value for the probable reliability of that result. For methods of such calculation the student is referred to Goodwin's *Precision of Measurements.*

3. Significant Figures as a Means of Expressing Reliability.—In chemical computations the use of numerical precision measures for expressing reliability is usually inconvenient, for these precision measures are often difficult or impossible to determine. In such cases the reliability or precision of a numerical value is best indicated by the number of significant figures used in expressing that value. It is true that this method of expression gives only an approximate idea of the reliability of a result, but the importance of the retention of the proper number of significant figures in analytical data cannot be overemphasized. A numerical result expressed by fewer or more significant figures than are warranted by the various factors involved may give to an observer an impression nearly as erroneous as would be given by a result which is inaccurate.

4. Rules Governing the Use of Significant Figures in Chemical Computations.—The following definitions and rules are suggested by those given in Goodwin's *Precision of Measurements:*

A *number* is an expression of quantity.

A *figure*, or *digit*, is any one of the characters: 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, which, alone or in combination, serve to express numbers.

A *significant figure* is a digit which denotes the amount of the quantity in the place in which it stands. In the case of the number 243, the figures signify that there are two hundreds,

four tens, and three units, and are therefore all significant. The character, 0, is used in two ways. It may be used as a significant figure, or it may be used merely to locate the decimal point. It is a significant figure when it indicates that the quantity in the place in which it stands is known to be nearer zero than to any other value. Thus, the weight of a crucible may be found to be 10.603 grams, in which case all five figures, including the zeros, are significant. If the weight in grams of the crucible were found to be 10.610, meaning that the weight as measured was nearer 10.610 than 10.609 or 10.611, both zeros would be significant.

By analysis, the weight of the ash of a quantitative filter paper is found to be 0.00003 gram. Here none of the zeros are significant, but merely serve to show that the figure 3 belongs in the fifth place to the right of the decimal point. Any other characters except digits would serve the purpose as well. The same is true of the value 356,000 inches, when signifying the distance between two given points as measured by instruments which are accurate to three figures only. The zeros are not significant.

Rule I.—Retain as many significant figures in a result and in data in general as will give only one uncertain figure. (For very accurate work involving lengthy computations, two uncertain figures may sometimes be retained.) Thus, the value 25.34, representing the reading of an ordinary burette, contains the proper number of significant figures, for the digit 4 is obtained by estimating an ungraduated scale division, and is doubtless uncertain. Another observer would perhaps give a slightly different value for the burette reading—for example, 25.33 or 25.35. All four figures should be retained.

Rule II.—In rejecting superfluous and inaccurate figures, increase by 1 the last figure retained if the following rejected figure is 5 or over. Thus, in rejecting the last figure of the number 16.279, the new value becomes 16.28.

Rule III.—In adding or subtracting a number of quantities, extend the significant figures in each term and in the sum or difference only to the point corresponding to that uncertain figure occurring farthest to the left relative to the decimal point.

For example, the sum of the following three terms: 0.0121, 25.64, and 1.05782, assuming the last figure in each to be uncertain, is

$$\begin{array}{r} 0.01 \\ 25.64 \\ 1.06 \\ \hline 26.71 \end{array}$$

Here it is seen that the second term has its first uncertain figure (the 4) in the hundredths place, the following figures being unknown. Hence it is useless to extend the digits of the other terms beyond the hundredths place even though they are given to the ten thousandths place in the first term and to the hundred thousandths place in the third term. The third digit of the third term is increased by 1 in conformity with Rule II above. The fallacy of giving more than four significant figures in the sum may be shown by substituting x for each unknown figure. Thus,

$$\begin{array}{r} 0.0121x \\ 25.64xxx \\ 1.05782 \\ \hline 26.71xxx \end{array}$$

Rule IV.—In multiplication or division, the percentage precision of the product or quotient cannot be greater than the percentage precision of the least precise factor entering into the computation. Hence, in computations involving multiplication or division, or both, retain as many significant figures in each factor and in the numerical result as are contained in the factor having the largest percentage deviation. In most cases, as many significant figures may be retained in each factor and in the result as are contained in the factor having the least number of significant figures.

For example, the product of the three terms: 0.0121, 25.64, and 1.05782, assuming the last figure in each to be uncertain, is

$$0.0121 \times 25.6 \times 1.06 = 0.328,$$

for if the first term is assumed to have a possible variation of one in the last place, it has an actual deviation of one unit in every

121 units, and its percentage deviation would be $\frac{1}{121} \times 100 = 0.8$. Similarly, the possible percentage deviation of the second term would be $\frac{1}{2,564} \times 100 = 0.04$, and that of the third term would be $\frac{1}{105,782} \times 100 = 0.0009$. The first term, having the largest percentage deviation, therefore governs the number of significant figures which may be properly retained in the product, for the product cannot have a precision greater than 0.8 per cent. That is, the product may vary by 0.8 parts in every hundred or by nearly three parts in every 328. The last figure in the product as expressed with three significant figures above is therefore doubtful and the proper number of significant figures has been retained.

Rule V.—Computations involving a precision not greater than one-fourth of 1 per cent should be made with a 10-inch slide rule. For greater precision, logarithm tables should be used. If the old-style method of multiplication or division must be resorted to, reject all superfluous figures at each stage of the operation.

Rule VI.—In carrying out the operations of multiplication or division by the use of logarithms, retain as many figures in the mantissa of the logarithm of each factor as are properly contained in the factors themselves under Rule IV. Thus, in solving the example given under Rule IV, the logarithms of the factors are expressed as follows:

$$\begin{aligned} \log 0.0121 &= 8.083 - 10 \\ \log 25.64 &= 1.409 \\ \log 1.05782 &= 0.024 \\ & \overline{9.516 - 10} = \log 0.328 \end{aligned}$$

5. Solution of Numerical Problems.—In calculating numerical results from chemical data which have been obtained under known conditions and by known methods, little difficulty should be experienced in forming an approximate estimate of the reliability of the various factors and of the results obtained. In the case of numerical problems which are unaccompanied by any data to show the conditions under which the various measurements were made or the precision of the values given, the reten-

tion of the proper number of significant figures in the final computed results may be a matter of considerable judgment. In such cases the above rules are subject to modification, but in any case it should be remembered that the use of a certain amount of common sense and judgment in no way detracts from their value.

In answering problems in this book, it may be assumed that the given data conform to Rule I, above. In problems involving such statements as "a 2-gram sample," or "15 c.c. of titrating reagent," the precision obtainable with an ordinary chemical balance, burette, or other measuring apparatus is understood. Under such conditions, these values would be 2.0000 grams and 15.00 c.c. respectively, with the last figure uncertain in each case. Similarly, it may be assumed that the normality of a "tenth normal solution" is known to a precision at least as great as that of the other factors involved.

It often happens that independent calculations from given data give results which disagree only by one or two units in the last significant figure retained. This is usually due to the fact that figures have been rejected at different stages of the operations involved, but this is usually of no importance, since when properly expressed, the last significant figure in the result is doubtful anyway.

It should also be remembered that the atomic weights of the elements are known only to a limited number of significant figures, and in the absence of further data, it may be assumed that the values ordinarily given in atomic weight tables conform to Rule I above, in that the last figure in each is usually doubtful. It follows, therefore, that the same attention must be paid to the reliability of the atomic and molecular weights involved in computations as to that of any other data.

Problems

1. Samples were sent to seven different chemists to be analyzed for percentage of protein. The values reported were 43.18; 42.96; 42.88; 43.21; 43.01; 43.10; 43.08. What is the mean value, the average deviation of a single value from the mean, and the deviation of the mean?

Ans. 43.060; 0.094; 0.036.

2. How many significant figures are in the value 2.27×10^{-9}? In the value 5,000.002?

Ans. Three. Seven.

3. Assuming the last significant figure in each value to be uncertain, what per cent of 0.141729 is 0.0058?

Ans. 4.1 per cent.

4. One kilogram = 2.2046223+ pounds. In converting the value 0.3840 kilogram to pounds, knowing the last figure to be uncertain, what method should be used, and what is the numerical result?

Ans. Four-place logarithms; 0.8467 lb.

5. It is necessary to solve the following:

$(1.276 \times 0.00047) + (1.7 \times 10^{-4}) - (0.0021764 \times 0.0121)$ each term being uncertain in the last significant figure. Should you use arithmetic, logarithms, or a slide rule in the multiplications? What is the final answer?

Ans. Slide rule. 7.5×10^{-4}.

6. Two analysts working independently on the same sample of steel report duplicate analyses as follows:

Analyst 1: Sulphur = 0.042 per cent
0.040 per cent
Analyst 2: Sulphur = 0.04178 per cent
0.04176 per cent

Both men use a 3.5-gram sample weighed to the nearest tenth of a gram. Is Analyst 2 justified in his report? Do his figures necessarily indicate greater ability as an analyst?

Ans. No. No.

7. A value which has been found by two analyses to be 0.1129 and 0.1133 respectively is to be multiplied by 1.36 c.c. as measured by an ordinary burette, and the product is to be subtracted from the value 0.93742 which has been very accurately measured. Express the result by the proper number of significant figures.

Ans. 0.783.

CHAPTER II

CHEMICAL EQUATIONS

6. Purpose of Chemical Equations.—When the nature and composition of the initial and final products of a chemical reaction are known, the facts can be symbolized in the form of a chemica' equation. When properly written, the equation indicates (1) the nature of the atoms and the composition of the molecules taking part in the reaction; (2) the proportions by weight of the interacting and resulting substances; and (3) the proportions by volume of all gases involved. These three principles applied to reactions which go to completion serve as the foundation of Quantitative Chemical Analysis. Before the calculation of a chemical analysis can be made, it is necessary to understand the chemistry involved and to be able to express it in the form of balanced equations.

7. Writing and Balancing Equations.—The determination of the nature of the products formed by a given reaction involves a knowledge of general chemistry which, it is assumed, has already been acquired from previous study, but the ability to write and balance equations correctly and quickly is acquired by considerable practice. The following discussion is given to help the student attain proficiency, especially in regard to equations involving oxidation and reduction, which usually give the most trouble to the beginner.

With equations expressing the reactions of (1) combination, (2) decomposition, and (3) double decomposition, it is seldom that much difficulty is experienced in bringing about equality between the atoms and molecules of the reacting substances and those of the products, for little more is involved than purely mechanical adjustment of the terms and an elementary knowledge of valence. As examples of the above types of chemical change in the order given, the following equations may be cited:

(1) $2H_2 + O_2 \rightarrow 2H_2O$

(2) $2HgO \rightarrow 2Hg + O_2$

(3) $FeCl_3 + 3NH_4OH \rightarrow Fe(OH)_3 + 3NH_4Cl.$

Equations expressing reactions of oxidation and reduction, although usually somewhat more complicated, offer little additional difficulty provided the principles underlying these types of chemical change are thoroughly understood.

Oxidation is the increase in positive valence of an element or radical; reduction is the decrease in positive valence of an element or radical. Oxidation is always accompanied simultaneously by reduction, for a substance cannot be oxidized without causing a corresponding and equivalent reduction of the oxidizing agent.

A. Consider the reaction between ferrous chloride and chlorine, the unbalanced equation being written:

$$FeCl_2 + Cl_2 \rightarrow FeCl_3.$$

The valence of the iron increases *one* (from plus two to plus three). The valence of each chlorine atom changes from zero to minus one, or the valence of the chlorine *molecule* decreases *two*. Since oxidation and reduction must take place in the same degree, it is necessary to cross-multiply and take *two* ferrous chloride molecules to *one* chlorine molecule. After balancing, the equation then becomes:

$$2FeCl_2 + Cl_2 \rightarrow 2FeCl_3.$$

Since *any* ferrous salt will be oxidized by chlorine, the reaction may be better expressed in terms of the ions:

$$2Fe^{++} + Cl_2 \rightarrow 2Fe^{+++} + 2Cl^-.$$

B. The reaction between potassium dichromate and ferrous sulphate in sulphuric acid solution may be expressed by the unbalanced equation:

$$K_2Cr_2O_7 + FeSO_4 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + Fe_2(SO_4)_3 + H_2O.$$

The valence of each chromium atom in potassium dichromate is plus six, the valence of each chromium atom in chromic sulphate is plus three; the valence of iron in ferrous sulphate is plus two, and the valence of iron in ferric sulphate is plus three. The valence of each chromium atom therefore changes *three*. Since the dichromate radical contains two chromium atoms, the decrease in valence of the potassium dichromate is *six*. The valence of the iron increases *one*. Therefore to bring about equality, *six* ferrous sulphate molecules must be taken for *one*

molecule of potassium dichromate, and the equation becomes:

$$K_2Cr_2O_7 + 6FeSO_4 + H_2SO_4 \rightarrow$$
$$Cr_2(SO_4)_3 + K_2SO_4 + Fe_2(SO_4)_3 + H_2O,$$

in which only the $K_2Cr_2O_7$ and the $FeSO_4$ are balanced. With these two as a basis, the corresponding salts on the right-hand side of the equation are now balanced:

$$K_2Cr_2O_7 + 6FeSO_4 + H_2SO_4 \rightarrow$$
$$Cr_2(SO_4)_3 + K_2SO_4 + 3Fe_2(SO_4)_3 + H_2O.$$

It is now only necessary to balance the H_2SO_4 and the H_2O. To provide the proper number of sulphate radicals the coefficient of the H_2SO_4 must be seven, and to balance the hydrogen and oxygen atoms the coefficient of the H_2O must be seven. The equation becomes:

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \rightarrow$$
$$Cr_2(SO_4)_3 + K_2SO_4 + 3Fe_2(SO_4)_3 + 7H_2O.$$

Since *any* dichromate will be reduced by *any* ferrous salt in the presence of *any* acid, a more general equation may be written:

$$Cr_2O_7^{=} + 6Fe^{++} + 14H^{+} \rightarrow 2Cr^{+++} + 6Fe^{+++} + 7H_2O.$$

Equality is expressed between the atoms and between the electrical charges.

C. Knowing the valences which reacting elements or radicals commonly exhibit and the state of the solution in which the reaction takes place, it is usually a simple matter to express the complete skeleton equation representing the reaction. The equation may then be readily balanced. For example, it is known that potassium permanganate and stannous chloride will react in acid solution. The former, being an oxidizing agent, is reduced; the latter, being a reducing agent, is oxidized. The valence of manganese in potassium permanganate is +7; the valence of tin in stannous chloride is +2. Reduction of permanganate in acid solution always gives a manganous salt in which the valence of manganese is +2. The oxidation product of a stannous salt is always a stannic salt in which the valence of tin is +4. Assuming the acidity of the solution to be due to hydrochloric acid, the reaction may be written in outline form:

$$KMnO_4 + SnCl_2 + HCl \rightarrow MnCl_2 + SnCl_4 + KCl + H_2O.$$

Cross-multiplying the changes in valence of the oxidizing and reducing agents and balancing with these as a basis:

$2KMnO_4 + 5SnCl_2 + HCl \rightarrow 2MnCl_2 + 5SnCl_4 + 2KCl + H_2O.$

To complete the equation it is now only necessary to balance the HCl and H_2O:

$$2KMnO_4 + 5SnCl_2 + 16HCl \rightarrow 2MnCl_2 + 5SnCl_4 + 2KCl + 8H_2O.$$

D. When metallic copper is dissolved in dilute nitric acid, the reaction may be written according to the skeleton equation:

$$Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO + H_2O.$$

Here, the copper is oxidized, but only *part* of the nitric acid acts as an oxidizing agent, the remainder entering into reaction as an acid to form cupric nitrate. This dual character of the nitric acid may be expressed as follows:

$$\underset{\text{(oxidizing)}}{Cu + HNO_3 + HNO_3} \rightarrow Cu(NO_3)_2 + NO + H_2O.$$

Each atom of copper increases by two units of valence, while the nitrogen of the oxidizing agent decreases by three units. Therefore there must be *three* copper atoms to *two* oxidizing molecules of nitric acid:

$$\underset{\text{(oxidizing)}}{3Cu + 2HNO_3 + HNO_3} \rightarrow Cu(NO_3)_2 + NO + H_2O.$$

To balance with these as a basis, it is now necessary to take six nitric acid molecules as an acid to furnish the required nitrate radicals in combination with the copper. The equation becomes:

$$\underset{\text{(oxidizing)}}{3Cu + 2HNO_3 + 6HNO_3} \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O,$$

or $$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O.$$

The equation may also be written in ionic form according to the skeleton equation:

$$Cu^0 + NO_3^- + H^+ \rightarrow Cu^{++} + NO + H_2O,$$

which, after balancing, becomes:

$$3Cu^0 + 2NO_3^- + 8H^+ \rightarrow 3Cu^{++} + 2NO + 4H_2O.$$

In this case the ionic equation has the advantage over the molecular equation in that it not only shows the essential reacting

constituents, but also shows directly the proportion of the nitric acid required to oxidize the copper. Of every eight acid molecules, only two are oxidizing. Any acid can take the place of the remaining six, thus:

$$3Cu + 2HNO_3 + 3H_2SO_4 \rightarrow 3CuSO_4 + 2NO + 4H_2O.$$

Similarly, $3Ag^0 + NO_3^- + 4H^+ \rightarrow 3Ag^+ + NO + 2H_2O$,

and $Fe^0 + NO_3^- + 4H^+ \rightarrow Fe^{+++} + NO + 2H_2O$.

E. In the skeleton equation

$$Cu_2S + NO_3^- + H^+ \rightarrow Cu^{++} + S + NO + H_2O,$$

the valence of each copper atom increases one, and each sulphur atom two. The increase for the cuprous sulphide molecule is therefore four. Since the valence of the nitrogen decreases three, it is necessary to take three cuprous sulphide molecules for every four nitrate radicals. The coefficient for the hydrogen ion is then mathematically found to be 16, and the equation becomes:

$$3Cu_2S + 4NO_3^- + 16H^+ \rightarrow 6Cu^{++} + 3S + 4NO + 8H_2O,$$

or $3Cu_2S + 16HNO_3 \rightarrow 6Cu(NO_3)_2 + 3S + 4NO + 8H_2O$.

It should be borne in mind that the relative changes in valence provide a means of determining the *relative* number of molecules of the oxidizing and reducing substances. The coefficients thus determined may be increased or decreased in the same proportion to suit the case at hand. This is illustrated by the equation:

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \rightarrow K_2SO_4 + 5Fe_2(SO_4)_3 + 2MnSO_4 + 8H_2O$$

in which, although the ratio of the changes in valence is five to one, the coefficients of the potassium permanganate and ferrous sulphate molecules must be taken as 2 and 10 respectively in order to obtain whole numbers for the coefficients of the potassium sulphate and ferric sulphate molecules.

It should also be remembered that in writing ionic equations only highly ionized soluble substances are written in the ionic form. Insoluble substances and slightly ionized compounds are expressed in the molecular form.

The following table shows some of the changes in valence involved in reactions which are frequently encountered in general analytical work. It is intended to be illustrative rather than exhaustive.

Element	Molecular Change		Valence Change of Element
Antimony	$SbO_3^{=}$	$\rightarrow SbO_4^{=}$	+3 to +5
Arsenic	$AsO_3^{=}$	$\rightarrow AsO_4^{=}$	+3 to +5
Bromine	Br^-	$\rightarrow Br^0$	−1 to 0
	BrO_3^-	$\rightarrow Br^-$	+5 to −1
Carbon	$C_2O_4^{=}$*	$\rightarrow CO_2$	+2 to +4
Chlorine	Cl^-	$\rightarrow Cl^0$	−1 to 0
	ClO_3^-	$\rightarrow Cl^-$	+5 to −1
	ClO_3^-	$\rightarrow ClO_2$	+5 to +4
Chromium	$Cr_2O_7^{=}$	$\rightarrow Cr^{+++}$	+6 to +3
	$CrO_4^{=}$	$\rightarrow Cr^{+++}$	+6 to +3
Hydrogen	H^+	$\rightarrow H^0$	+1 to 0
Iodine	I^-	$\rightarrow I^0$	−1 to 0
	IO_3^-	$\rightarrow I^-$	+5 to −1
	IO_4^-	$\rightarrow I^-$	+7 to −1
Iron	Fe^{++}	$\rightarrow Fe^{+++}$	+2 to +3
Manganese	MnO_4^-	$\rightarrow Mn^{++}$	+7 to +2
	MnO_4^-	$\rightarrow MnO_2$	+7 to +4
	MnO_2	$\rightarrow Mn^{++}$	+4 to +2
Molybdenum	$MoO_4^{=}$	$\rightarrow MoO_2^-$	+6 to +3
Nitrogen	NO_3^-	$\rightarrow NO$	+5 to +2
	NO_3^-	$\rightarrow NO_2$	+5 to +4
	NO_2^-	$\rightarrow NO_3^-$	+3 to +5
Oxygen	H_2O_2*	$\rightarrow H_2O$	0 to −2
	H_2O_2*	$\rightarrow O_2$	−2 to 0
Sulphur	$S^=$	$\rightarrow S^0$	−2 to 0
	$S^=$	$\rightarrow SO_3^=$	−2 to +4
	$S^=$	$\rightarrow SO_4^=$	−2 to +6
	$SO_3^=$	$\rightarrow SO_4^=$	+4 to +6
	S^0	$\rightarrow SO_4^=$	0 to +6
Tin	Sn^{++}	$\rightarrow Sn^{++++}$	+2 to +4
Vanadium	$V_2O_2^{++++}$	$\rightarrow VO_3^-$	+4 to +5

* In the case of carbon in $C_2O_4^=$ and oxygen in H_2O_2, the element in question exists in two valences of which only one undergoes change. Explanation of these cases is given on pages 126 and 127.

Problems

8. Balance the following metathetical reactions: (*a*) $H_2PtCl_6 + KCl \rightarrow HCl + K_2PtCl_6$; (*b*) $K_2PtCl_6 \rightarrow KCl + Pt + Cl_2$; (*c*) $AlCl_3 + KOH \rightarrow KCl + KAlO_2$; (*d*) $Pb(OH)_2 + KOH \rightarrow K_2PbO_2 + H_2O$; (*e*) $Cd(CN)_2 + KCN \rightarrow K_2Cd(CN)_4$; (*f*) $H_3PO_4 + (NH_4)_2MoO_4 + HNO_3 \rightarrow (NH_4)_3PO_4 . 12MoO_3 + NH_4NO_3 + H_2O$; (*g*) $(NH_4)_3PO_4 . 12MoO_3 + NH_4OH \rightarrow (NH_4)_3PO_4 + (NH_4)_2MoO_4 + H_2O$.

9. Balance the following ionic equations: (*a*) $Ba^{++} + SO_4^= \rightarrow BaSO_4$; (*b*) $Al^{+++} + OH^- \rightarrow AlO_2^- + H_2O$; (*c*) $Ag^+ + CN^- \rightarrow Ag(CN)_2^-$; (*d*)

$Cd(CN)_4^{=} + H_2S \rightarrow CN^- + H^+ + CdS$; (*e*) $Sn^{++++} + H_2S \rightarrow SnS_2 + H^+$; (*f*) $Fe^{+++} + [Fe(CN)_6]^{\equiv} \rightarrow Fe_4[Fe(CN)_6]_3$; (*g*) $AsS_3^{=} + H^+ - As_2S_3 + H_2S$.

10. Balance the following oxidation and reduction equations: (*a*) $KMnO_4 + H_2O_2 + H_2SO_4 \rightarrow KHSO_4 + MnSO_4 + H_2O + O_2$; (*b*) $KI + H_2O_2 \rightarrow KOH + I_2$; (*c*) $AlCl_3 + Na_2S_2O_3 + H_2O \rightarrow NaCl + S + SO_2 + Al(OH)_3$; (*d*) $CrCl_3 + NaC_2H_3O_2 + H_2O + Cl_2 \rightarrow NaCl + HC_2H_3O_2 + Na_2CrO_4$; (*e*) $K_2Cr_2O_7 + FeCl_2 + HCl \rightarrow KCl + FeCl_3 + CrCl_3 + H_2O$; (*f*) $KMnO_4 + MnSO_4 + H_2O \rightarrow K_2SO_4 + MnO_2 + H_2SO_4$; (*g*) $Au + HNO_3 + HCl \rightarrow H_2O + NO + AuCl_3$.

11. Balance the following oxidation and reduction equations: (*a*) $Fe^{++} + ClO_3^- + H^+ \rightarrow Fe^{+++} + Cl^- + H_2O$; (*b*) $Cr^{+++} + MnO_2 + H_2O \rightarrow Mn^{++} + CrO_4^{=} + H^+$; (*c*) $MnO_4^- + Cl^- + H^+ \rightarrow Mn^{++} + Cl_2 + H_2O$; (*d*) $MnO_4^- + H_2S + H^+ \rightarrow Mn^{++} + S + H_2O$; (*e*) $IO_3^- + I^- + H^+ \rightarrow I_2 + H_2O$.

12. Write balanced ionic equations for each of the following reactions taking place in solution. Introduce acid and water wherever necessary. (*a*) Dichromate reduced by sulphite giving chromic salt and sulphate; (*b*) chromic salt oxidized by free chlorine to give chromate and chloride; (*c*) chromite oxidized with sodium peroxide to chromate; (*d*) lead peroxide oxidized by permanganate giving manganous salt and free oxygen; (*e*) cupric salt and metallic aluminum giving aluminum salt and metallic copper; (*f*) manganous salt and chlorate giving a precipitate of manganese dioxide and chlorine dioxide gas; (*g*) cobaltous chloride in alkaline solution with hydrogen peroxide to give a precipitate of cobaltic hydroxide.

13. Express the following reactions in ionic form and in each case state what fraction of the nitric acid employed serves for oxidation: (*a*) $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + H_2O$; (*b*) $Zn + HNO_3 \rightarrow Zn(NO_3)_2 + NO + H_2O$; (*c*) $Cu_2S + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + H_2SO_4 + H_2O$; (*d*) $Cu_2S + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + S + H_2O$; (*e*) $FeS + HNO_3 \rightarrow Fe(NO_3)_3 + S + NO + H_2O$; (*f*) $FeS + HNO_3 \rightarrow Fe(NO_3)_3 + NO_2 + H_2SO_4 + H_2O$; (*g*) $Sn + HNO_3 \rightarrow H_2SnO_3 + NO + H_2O$.

CHAPTER III

THE CHEMICAL BALANCE

8. Sensitiveness of the Chemical Balance.—The determination of the weight or the mass of a body is a fundamental measurement of analytical chemistry, and is almost invariably made with an equal arm balance of high degree of precision. An equal arm balance consists essentially of a rigid beam supported horizontally at its center on a knife edge and so loaded at its ends with balance-pans that the center of gravity of the swinging portion is below the point of support.

The sensitiveness or sensitivity of a chemical balance is the tangent of the angle through which the pointer is displaced by a small excess load (usually 1 milligram) on the balance-pan. This angle is usually so small that it is sufficiently accurate to define the sensitiveness of a balance as the number of scale divisions through which the zero point of the balance is displaced by an excess load of 1 milligram.

The sensitiveness varies directly with the length of the balance-beam, inversely as the weight of the beam, and inversely as the distance between the center of gravity of the swinging portion and the point of support. That is,

$$tan\ \alpha = \frac{l}{bd}k,$$

in which α is the angle through which the pointer is moved; b is the weight of the beam; l, the length of the beam; d, the distance between the center of gravity and the point of support; and k is a constant.

9. Conversion of Weight in Air to Weight in Vacuo.—Archimedes' Principle states that any substance immersed in a fluid weighs less by an amount equal to the weight of fluid displaced. Consequently, a substance weighed in the ordinary manner is buoyed up to a slight extent by the surrounding air, and for accurate determinations, especially those involving the weighing

of objects of large volume, a correction for this buoyant effect must be applied. Since the usual method of weighing consists in balancing the substance to be weighed against standard weights, the surrounding air likewise exerts a buoyant effect upon the weights. If the volume occupied by the weights used is equal to the volume occupied by the substance, the buoyant effects will be equal, and the weight of the substance in vacuo will be the same as its weight in air. If the volume occupied by the substance is greater than the volume occupied by the weights, the substance will weigh more in vacuo than in air; and if the weights have the greater volume, the substance will weigh less in vacuo than in air. In any case, the difference between the weight in air and the weight in vacuo will be equal to the difference between the weight of the air displaced by the substance and the weight of the air displaced by the weights used. The weight in vacuo, W^0, may be expressed by the equation $W^0 = W + (V - V')a$,
in which

W = the weight of a substance in air,
V = the volume occupied by the substance,
V' = the volume occupied by the weights used,
and
a = the weight of a unit volume of air.

Since in practice, the volume occupied by the substance and the volume occupied by the weights are usually unknown, the formula is better written by expressing the values V and V' in terms of weight and specific gravity. If s is the specific gravity of the substance, and s' the specific gravity of the weights, the volume occupied by the substance will be $\frac{W^0}{s}$, and the volume occupied by the weights used will be $\frac{W}{s'}$. The formula may now be written:

$$W^0 = W + \left(\frac{W^0}{s} - \frac{W}{s'}\right)a.$$

Since the value following the plus sign in this expression is small compared to the value W to which it is added, and since W and W^0 are nearly equal, W may be substituted for the W^0 in

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of objects of large volume, a correction for this buoyant effect must be applied. Since the usual method of weighing consists in balancing the substance to be weighed against standard weights, the surrounding air likewise exerts a buoyant effect upon the weights. If the volume occupied by the weights used is equal to the volume occupied by the substance, the buoyant effects will be equal, and the weight of the substance in vacuo will be the same as its weight in air. If the volume occupied by the substance is greater than the volume occupied by the weights, the substance will weigh more in vacuo than in air; and if the weights have the greater volume, the substance will weigh less in vacuo than in air. In any case, the difference between the weight in air and the weight in vacuo will be equal to the difference between the weight of the air displaced by the substance and the weight of the air displaced by the weights used. The weight in vacuo, W^0, may be expressed by the equation $W^0 = W + (V - V')a$,
in which

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V = the volume occupied by the substance,
V' = the volume occupied by the weights used,
and
a = the weight of a unit volume of air.

Since in practice, the volume occupied by the substance and the volume occupied by the weights are usually unknown, the formula is better written by expressing the values V and V' in terms of weight and specific gravity. If s is the specific gravity of the substance, and s' the specific gravity of the weights, the volume occupied by the substance will be $\frac{W^0}{s}$, and the volume occupied by the weights used will be $\frac{W}{s'}$. The formula may now be written:

$$W^0 = W + \left(\frac{W^0}{s} - \frac{W}{s'}\right)a.$$

Since the value following the plus sign in this expression is small compared to the value W to which it is added, and since W and W^0 are nearly equal, W may be substituted for the W^0 in

the parenthesis without appreciably affecting the accuracy of the formula:

$$W^0 = W + \left(\frac{W}{s} - \frac{W}{s'}\right)a$$

or,

$$W^0 = W + W\left(\frac{a}{s} - \frac{a}{s'}\right).$$

Although the value of a varies slightly with the temperature and barometric pressure, the approximate value of 0.0012 gram for the weight of one cubic centimeter of air may be used except in cases where extreme accuracy is required, or where the atmospheric conditions are highly abnormal. Accurate values of a are given in Table III (Appendix). See also Table II for the specific gravities of common substances. A consideration of the precision of the various terms shows that the values of a, s, and s' need be known only approximately, and that in most cases the computation may be performed with sufficient accuracy by means of a slide rule.

Example I.—A platinum crucible weighs 25.6142 grams in air against brass analytical weights. What is its weight in vacuo?

Specific gravity of platinum = 21.37 = s
Specific gravity of brass weights = 8.0 = s'
Weight of 1 c.c. of air = 0.0012 gram = a.

Substituting in the above formula,

$$W^0 = 25.6142 + \left(\frac{25.6142}{21.37} - \frac{25.6142}{8.0}\right)0.0012$$
$$= 25.6142 + \left(\frac{26}{21} - \frac{26}{8.0}\right)0.0012$$
$$= 25.6142 - 0.0024$$
$$= 25.6118 \text{ grams.} \quad Ans.$$

10. Calibration of Balance Weights.—Since the fundamental operation of Quantitative Analysis is that of weighing, the calibration of balance weights is a process which should always precede careful analytical work. For purposes of analytical work it is only necessary that the weights be in correct proportion to one another. That is, it is not necessary that the mass of the "10-gram" weight be exactly 10 grams so long as it is exactly twice the mass of the "5-gram" weight, and so on. This is the

principle on which the procedure for the calibration of weights is based. The following procedure is given in some detail because it is not always included in text books on Quantitative Analysis which this book is intended to supplement, and because the method is rapid and simple.

Since it is not always true that the arms of a chemical balance are of exactly equal length it is necessary in such a careful operation as the calibration of weights to weigh by the method of substitution. When substances A and B are compared to each other by this method, A is placed on the left-hand pan and a tare T is placed on the right-hand pan of such magnitude as to bring the beam to a point of equilibrium. A is then replaced by B using the same tare on the right-hand pan. If the balance comes to the same point of equilibrium, the masses of A and B are equal. If there is a difference between the two, that difference may be determined as the small weight necessary to add to or subtract from either side to bring the balance to the same point of equilibrium. For a tare, bits of paper or of sand may be used, or more conveniently, an auxiliary set of weights. It is well to include the rider (on the beam) with the tare, for in this way the change in position of the rider on the beam is a direct measure of the difference in mass between the two substances weighed.

The box of weights always contains some weights of the same denomination. These must be marked or characteristics noted so that they may be distinguished from each other. Place one of the 0.01 gram weights on the left-hand pan and a tare of lesser value on the right-hand pan and by means of the rider on the beam bring to equilibrium; for example with the rider at 5.2 milligrams. This 0.01 gram weight is temporarily taken as the standard and assumed to be exactly 0.0100 gram. Remove this centigram weight and replace it by the other centigram weight (0.01′). By means of the rider bring to the same point of equilibrium as before. The distance the rider has been moved gives directly the difference in mass between these two centigram weights. The value of the second weight may therefore be expressed in terms of the first (the assumed standard). If in the second case the rider is at 5.4 milligrams the mass of the second weight is 0.0102 gram. Similarly find the value of a

third centigram weight (0.01″) in terms of the standard. Now place the 0.01 and 0.01′ weights on the left-hand pan, a tare of about 0.015 gram on the right-hand pan and balance with the rider (for example at 4.9 milligrams). Replace the 0.01 + 0.01′ by the 0.02 weight and determine again the position of the rider. Suppose this to be at 5.1 milligrams. The value of the 0.02 weight is 0.0100 + 0.0102 + 0.0002 = 0.0204 gram. Now place the 0.02 + 0.01 + 0.01′ + 0.01″ weights on the left-hand pan and a tare of about 0.045 gram on the right-hand pan and bring to equilibrium with the rider. Replace the weights by the 0.05 weight, again note the change in position, and determine the comparative value of the 0.05 weight as above. Proceed in this way with all the weights in the box in increasing order, always by the method of tares, balancing each weight against the sum of smaller weights. Include in the weighings a 10-gram Bureau of Standards weight if available. Tabulate the values obtained against the face value of each weight (see example below).

By the above procedure the values obtained would be consistent among themselves, but the corrections may be large on account of the small standard taken. Therefore it is best to convert all these corrections to a 10-gram standard. One of the 10-gram box weights may be taken for this standard for it is only necessary that the weights be in correct proportion. But by taking a Bureau of Standards weight for the standard, the true mass of each weight is determined, thus allowing interchange of weights from other boxes similarly standardized. The next step, therefore, is to convert the values obtained above to the new chosen standard. To do this find the aliquot part of the mass of the standard 10-gram weight corresponding to the face value of each weight. Thus in the example given below, the standard 10-gram weight in terms of the 0.01-gram standard is 10.0176 grams. The 5-gram weight should weigh one-half of this or 5.0088 grams, etc. The correction to be applied in each case is therefore simply the difference between the aliquot value of the 10-gram standard and the value found against the small standard.

Example I.—The following tabulation is that of only a few of the weights in a set and is given to show typical values obtained by the above method.

Face value	Balanced against	Rider movement	Mass (0.01 gram standard)	Aliquot part of 10-gram value	Correction in milligrams
0.01	temporary standard	.....	0.0100	0.0100	0.0
0.01′	0.01	+0.0002	0.0102	0.0100	+0.2
0.01″	0.01	+0.0001	0.0101	0.0100	+0.1
0.02	0.01+0.01′	−0.0001	0.0201	0.0200	+0.1
0.05	0.02+0.01+0.01′+0.01″	−0.0001	0.0503	0.0501	+0.2
2.0	1.0 +0.50+ etc	etc.	2.0034	2.0035	−0.1
5.0	2.0 + etc	etc.	5.0086	5.0088	−0.2
10.0	5.0 + etc	etc.	10.0175	10.0176	−0.1
10.0′	5.0 + etc	etc.	10.0176	10.0176	0.0
20.0	10.0 + etc	etc.	20.0356	20.0352	+0.4

Problems

14. The addition of a small weight to a certain balance displaces the pointer through an angle of 6°. Through what angle would a weight one and one-half times as great displace it?

Ans. 8° 57′.

15. A sample of an alloy having a volume of 2 c.c. is weighed in air with brass weights and is found to weigh 16.0000 grams. What is its weight in vacuo?

Ans. 16.0000 grams.

16. Find the weight in vacuo of a piece of gold which weighs 35.0000 grams in air against brass weights.

Ans. 34.9968 grams.

17. A substance weighing 12.3456 grams in air has a volume of 2 c.c. and a specific gravity equal to three times that of the weights used. What does it weigh in vacuo?

Ans. 12.3408 grams.

18. A quartz crucible weighing 16.0053 grams in a vacuum would weigh how many grams in air against brass weights?

Ans. 16.0005 grams.

19. A sample of brass weighs 12.8150 grams in air using platinum weights. What is its weight in vacuo?

Ans. 12.8162 grams.

20. A platinum crucible in air against brass weights weighs 15.1234 grams. What percentage error would be introduced in a multiplication if this value were used instead of the true mass of the crucible?

Ans. 0.01 per cent.

21. If a piece of gold in a vacuum weighs 35 times as much as a 1-gram brass weight in a vacuum, what would the brass weight weigh in air against

gold weights? What would the piece of gold weigh in air against brass weights?

Ans. 0.99991 gram; 35.0031 grams.

22. If with a temporary 0.010-gram standard the weight of a 20-gram balance weight is found to be 20.0186 grams and that of a 10-gram weight is found to be 10.0097 grams, what is the correction to be applied to the 20-gram weight if the 10-gram weight is taken as the standard? What is the correction to be applied to the 10-gram weight if the 20-gram weight is taken as the standard?

Ans. −0.8 mgs.; +0.4 mgs.

CHAPTER IV

EQUILIBRIUM CONSTANTS

11. Law of Mass Action.—The law of mass action applied to solutions states that when reacting substances are in equilibrium, the product of the concentrations of the substances formed, each raised to a power equal to the coefficient of its formula in the chemical equation, divided by the product of the concentrations of the reacting substances, each raised to a power equal to the coefficient of its formula in the equation, is a constant. Thus, in the general reaction

$$aA + bB + \ . \ . \ . \ = dD + eE + \ . \ . \ . \ ,$$

the law of mass action may be formulated as follows:

$$\frac{(D)^d(E)^e}{(A)^a(B)^b} = K,$$

in which the concentration of each substance is expressed by enclosing the symbol of that substance in parenthesis.

Although in computations involving chemical equilibria, concentrations are often expressed in terms of the number of moles (molecular weight in grams) of substance per liter of *solvent*, for dilute solutions this is practically the same as the number of moles per liter of *solution*, and as the latter is consistent with the definition of a molal solution as used in analytical computations, we shall employ it in formulating mass action expressions as well. In mass action expressions molal concentration is usually represented as above by enclosing in parenthesis the symbol of the element, compound, or radical in question.

12. Ionization Constant.—The mass action law can be applied to the equilibrium between the molecules of a weak acid or weak base and its ions. Thus, acetic acid is ionized in solutions as follows:

$$HC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^-.$$

Therefore,

$$\frac{(H^+)(C_2H_3O_2^-)}{(HC_2H_3O_2)} = K$$

That is, in a solution containing acetic acid, the total concentration of hydrogen ions (from whatever source) multiplied by the total concentration of acetate ions (from whatever source) divided by the concentration of un-ionized acetic acid, is a constant. This value is called the ionization constant of acetic acid. The mass action law does not apply generally to the ionization of strong acids, strong bases, or salts. It applies to them with fair approximation only at very low concentrations.

EXAMPLE I.—The ionization constant of acetic acid is 1.8×10^{-5}. What is the concentration of hydrogen ions in a tenth normal solution of the acid?

Tenth normal $HC_2H_3O_2$ = tenth molal $HC_2H_3O_2$.

Let x = molal concentration of H^+ ions,
Then x = molal concentration of $C_2H_2O_2^-$ ions,
and $0.1 - x$ = molal concentration of undissociated $HC_2H_3O_2$.

Therefore,

$$\frac{(x)(x)}{(0.1 - x)} = 1.8 \times 10^{-5}$$

Solving, $x = 1.3 \times 10^{-3}$ moles per liter. *Ans.*

Numerical values in mass action expressions should not be expressed to more than two significant figures. Therefore simplying assumptions can often be made. Thus in the above equation, the value of x is so small compared to the value 0.1 from which it is subtracted that it is well within the limit of precision to write $\frac{(x)(x)}{(0.1)} = 1.8 \times 10^{-5}$ and thus avoid solving a quadratic equation.

EXAMPLE II.—What is the hydrogen-ion concentration in 500 c.c. of a 0.1 molal solution of acetic acid containing an additional 2 grams of acetate ions added in the form of sodium acetate?

Two grams $C_2H_3O_2^-$ per 500 c.c. = 0.068 moles per liter.

Let x = concentration of H^+ ions
Then $x + 0.068$ = concentration of $C_2H_3O_2^-$ ions
and $0.1 - x$ = concentration of un-ionized $HC_2H_3O_2$.

$$\frac{(x)(x + 0.068)}{(0.1 - x)} = 1.8 \times 10^{-5},$$

or approximately, $\frac{(x)(0.068)}{(0.1)} = 1.8 \times 10^{-5}$ (since x is small). Solving, $x = 2.6 \times 10^{-5}$. *Ans.*

13. Polybasic Acids.—Polybasic acids like H_2S, H_2CO_3, H_3PO_4, etc. ionize in steps and a mass action expression can be written for each step. Thus, H_2S ionizes to form H^+ and HS^- in which case the ionization constant is

$$\frac{(H^+)(HS^-)}{(H_2S)} = K_1 = 9.1 \times 10^{-8}.$$

The HS^- ions are further ionized into H^+ and $S^=$, in which case

$$\frac{(H^+)(S^=)}{(HS^-)} = K_2 = 1.2 \times 10^{-15}.$$

Multiplying the two equations one by the other gives:

$$\frac{(H^+)^2(S^=)}{(H_2S)} = K = 1.1 \times 10^{-22}.$$

A *saturated* solution of H_2S is about 0.1 molal and $(H_2S) = 0.1$. Therefore in cases where metallic elements are precipitated by saturating their solutions with H_2S, $(H^+)^2(S^=) = 1.1 \times 10^{-23}$.

It is seen that the primary ionization of H_2S is much greater than the secondary ionization and that the ionization cannot be correctly expressed by the equation $H_2S \rightleftarrows 2H^+ + S^=$. The concentration of H^+ ions in a pure solution of H_2S is not twice that of the $S^=$ ions. In general the primary ionization of any polybasic acid is much greater than the secondary ionization.

EXAMPLE I.—What is the approximate hydrogen-ion concentration in a solution of hydrogen sulphide which is 0.07 molal in H_2S?

In solving this problem the expression $\frac{(H^+)^2(S^=)}{H_2S} = 1.1 \times 10^{-22}$ cannot be used since neither (H^+) nor $(S^=)$ is known and there is no simple relation between them. On the other hand, although H_2S is ionized in two steps the first ionization is so much greater than the second ionization that for the purpose of obtaining an approximate answer, the latter may be considered negligible. In other words, practically all of the hydrogen ions may be considered to come from the ionization of H_2S into H^+ and HS^-. Therefore (H^+) and (HS^-) are practically equal in value and

$$\frac{(H^+)(HS^-)}{H_2S} = 9.1 \times 10^{-8}$$

or

$$\frac{(x)(x)}{0.07} = 9.1 \times 10^{-8}$$

where

$$x = 8 \times 10^{-5} \text{ moles per liter.} \quad \textit{Ans.}$$

EXAMPLE II.—What is the concentration of $S^=$ ions in 200 c.c. of a solution which is 0.05 molal in H_2S and which by the addition of HCl contains a total of 0.12 equivalents of H^+ ions?

Let x = molal concentration of $S^=$ ions.

$0.05 - x$ = approx. 0.05 = concentration of undissociated H_2S.

$0.12 \times 5 = 0.6$ = concentration of H^+ ions.

$$\frac{(0.6)^2(x)}{(0.05)} = K = 1.1 \times 10^{-22}$$

$$x = 1.5 \times 10^{-23} \text{ moles per liter.} \quad \textit{Ans.}$$

The ionization constants of some of the more common weak acids and bases at room temperature are given in Table XII, Appendix.

14. Solubility Product.—In a saturated solution of a slightly soluble salt the concentration of the un-ionized molecules is itself a constant and the mass action expression can be simplified. Thus, in a solution saturated with AgCl, the ionization constant is

$$\frac{(Ag^+)(Cl^-)}{(AgCl)} = K.$$

The addition of Ag^+ ions or Cl^- ions to the solution causes some of the Ag^+ and Cl^- ions to form un-ionized AgCl so that K may keep its constant value. Since the solution is already saturated with the salt, the AgCl formed will separate from solution and the concentration of un-ionized AgCl in solution will be the same as before. That is, in a saturated solution of AgCl the concentration of un-ionized AgCl is a constant. The equilibrium expression can therefore be written simply

$$(Ag^+)(Cl^-) = K_s$$

and such a constant *which applies only to a saturated solution* is called the *solubility product* of the salt in question.

EXAMPLE I.—What is the solubility product of Ag_3PO_4 if the solubility of the salt is 6.5×10^{-3} gram per liter?

6.5×10^{-3} gram per liter $= \frac{6.5 \times 10^{-3}}{418.7} = 1.6 \times 10^{-5}$ mole per liter. The salt can be considered to be 100 per cent ionized as follows:

$$Ag_3PO_4 \rightarrow 3Ag^+ + PO_4^{\equiv}$$

Therefore, $(Ag^+) = 3 \times 1.6 \times 10^{-5}$

$$(PO_4^{\equiv}) = 1.6 \times 10^{-5}$$

$$(3 \times 1.6 \times 10^{-5})^3(1.6 \times 10^{-5}) = 1.8 \times 10^{-18}. \quad \textit{Ans.}$$

EXAMPLE II.—The solubility product of CaF_2 is 3.2×10^{-11}. How many grams of Ca^{++} are present in 500 c.c. of a saturated solution of CaF_2? How many grams of $CaCl_2$ can be dissolved in 500 c.c. of a solution containing 9.5 grams of fluoride ions?

Let x = molal concentration of Ca^{++}

Then $2x$ = molal concentration of F^-

$$(x)(2x)^2 = 3.2 \times 10^{-11}$$

$$x = 2.0 \times 10^{-4} \text{ mole per liter.}$$

$2.0 \times 10^{-4} \times 40 \times \frac{1}{2} = 0.004$ gram Ca^{++} per 500 c.c. *Ans.*

9.5 grams F^- per 500 c.c. = 1 mole F^- per liter.

$$(x)(1)^2 = 3.2 \times 10^{-11}$$

$$x = 3.2 \times 10^{-11} \text{ mole } Ca^{++} \text{ per liter.}$$

$3.2 \times 10^{-11} \times 111 = 2.9 \times 10^{-9}$ gram $CaCl_2$ per liter. *Ans.*

EXAMPLE III.—The solubility product of CdS $= 3.6 \times 10^{-29}$. How many grams of Cd can remain in the 200 c.c. of acidified solution of H_2S discussed in Example II of the preceding section?

$$(Cd^{++})(S^{\equiv}) = 3.6 \times 10^{-29}$$

$$(S^{\equiv}) = 1.5 \times 10^{-23}$$

Solving, $(Cd^{++}) = 2.4 \times 10^{-6}$ mole per liter.

$2.4 \times 10^{-6} \times 112 \times 0.2 = 5.4 \times 10^{-5}$ gram per 200 c.c. *Ans.*

Problems

23. Formic acid is a mono-basic acid which is 3.2 per cent ionized in 0.2 molal solution. What is the ionization constant of formic acid and what is its percentage ionization in 0.05 molal solution?

Ans. 2.1×10^{-4}; 6.4 per cent.

24. What is the approximate concentration of sulphide ions in a 0.07 molal solution of hydrogen sulphide?

Ans. 1.2×10^{-15} molal.

25. What is the concentration of an ammonium hydroxide solution which is 3.0 per cent ionized? Which is 0.5 per cent ionized?

Ans. 0.02 molal; 0.72 molal.

26. What is the hydrogen-ion concentration in a tenth normal acetic acid solution containing one mole of sodium acetate (85 per cent ionized) per liter?

Ans. 2.1×10^{-6} molal.

27. What are the hydrogen-ion and hydroxide-ion concentrations in a 0.01 molal solution of hypochlorous acid at 25° C.?

Ans. 2×10^{-5} molal; 5×10^{-10} molal.

28. Compute the concentration of sulphide ions in a solution which is 0.08 molal in H_2S and 0.15 normal in HCl assuming the latter to be 90 per cent ionized.

Ans. 4.9×10^{-22} molal.

29. If 0.00011 gram of silver bromide dissolves in one liter of water what is the solubility product of silver bromide?

Ans. 3.5×10^{-13}.

30. If the solubility product of lead phosphate is 1.5×10^{-32} how many milligrams will dissolve in 500 c.c. of water?

Ans. 0.070 mg.

31. If the solubility product of CaF_2 is 3.5×10^{-11}, what is the concentration of calcium ions in a saturated solution of CaF_2? What is the concentration of the calcium ions that can be present in a liter of solutions already containing 3 moles of fluoride ions?

Ans. 2.1×10^{-4} molal; 3.9×10^{-12} molal.

32. The solubility product of PbI_2 is 1.4×10^{-8}. How many grams of lead ions and of iodide ions are contained in each cubic centimeter of a saturated solution of lead iodide?

Ans. 3.1×10^{-4}; 3.8×10^{-4} gram.

33. If the solubility product of $Fe(OH)_3$ is 1.1×10^{-36} compute the weight of Fe^{+++} in milligrams which must be present in one liter of solution in order to cause precipitation of the hydroxide when the hydroxide-ion concentration is 8×10^{-5} moles per liter.

Ans. 1.2×10^{-19} mg.

34. What is the solubility product of $MgNH_4PO_4$ if 4.3 milligrams dissolve in 500 c.c. of water? How many milligrams would dissolve in 500 c.c. of a solution which is 0.1 molal in Mg^{++} ions and 0.5 molal in NH_4^+ ions?

Ans. 2.5×10^{-13}; 3.4×10^{-7} mg.

35. The solubility product of CdS is 3.6×10^{-29}, that of ZnS is 1.2×10^{-23}. Compute the number of grams of zinc and of cadmium which can remain dissolved in 1,500 c.c. of a solution which contains 0.05 mole of dissolved H_2S and is 0.3 N in hydrogen ions.

Ans. 29.0; 1.5×10^{-4} gram.

36. By saturating with hydrogen sulphide 350 c.c. of a solution which is 0.01 molal in a certain trivalent element and 1 molal in hydrogen ions, all but 0.00024 millimole of the element precipitates as sulphide. What is the approximate solubility product of the sulphide of the element?

Ans. 6.4×10^{-82}.

CHAPTER V

CALCULATIONS OF GRAVIMETRIC ANALYSIS

15. The Law of Definite Proportions Applied to Calculations of Gravimetric Analysis.—Gravimetric Analysis is based on the Law of Definite Proportions which states that in any pure compound the proportions by weight of the constituent elements are always the same, and on the Law of Constancy of Composition, which states that masses of the elements taking part in a given chemical change always exhibit a definite and invariable ratio to each other. It consists in determining the proportionate amount of an element, radical, or compound present in a sample by eliminating all interfering substances and converting the desired constituent or component into a weighable compound of definite, known composition. Having then determined the weight of this isolated compound, the weight of the desired component present in the sample may be readily calculated.

EXAMPLE I.—A sample of sodium chloride is dissolved in water and the chloride is precipitated with silver nitrate according to the reaction:

$$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3,$$

furnishing 1.0000 gram of silver chloride. What is the weight of chlorine in the original sample?

Since silver chloride always contains silver and chlorine in the respective ratio of their atomic weights, or in the ratio of 107.88 to 35.46, in every 143.34 (= 107.88 + 35.46) grams of silver chloride there are 35.46 grams of chlorine. In 1 gram of silver chloride there is $1 \times \frac{Cl}{AgCl} = 1 \times \frac{35.46}{143.34}$, = 0.2474 gram of chlorine. *Ans.*

16. Calculations from Equations.—A chemical equation not only represents the chemical changes taking place in a given reaction, but it also expresses the relative quantities of the substances involved. Thus, the equation:

$$H_2SO_4 + BaCl_2 \rightarrow BaSO_4 + 2HCl,$$

not only states that sulphuric acid reacts with barium chloride to give barium sulphate and hydrochloric acid, but it also expresses the fact that every 98.08 parts by weight of sulphuric acid react with 208.29 parts of barium chloride to give 233.43 parts of barium sulphate and 72.94 parts of hydrogen chloride, these numerical values being the molecular weights of the respective compounds. These are relative weights and are independent of the units chosen. If a weight of any one of the above four substances is known, the weight of any or all of the other three may be calculated by simple proportion. This is the basis of analytical computations.

EXAMPLE I.—The iron in a sample of $FeCO_3$ is converted by solution, oxidation, precipitation, and ignition into Fe_2O_3 weighing 1.0000 gram. What is the weight of iron expressed as $FeCO_3$, as Fe, and as FeO in the original sample?

The reactions may be expressed by the equations:

$$FeCO_3 + 2HCl \rightarrow FeCl_2 + CO_2 + H_2O$$
$$2FeCO_3 + 4HCl \rightarrow 2FeCl_2 + 2CO_2 + 2H_2O$$
$$2FeCl_2 + Br_2 + 2HCl \rightarrow 2FeCl_3 + 2HBr$$
$$2FeCl_3 + 6NH_4OH \rightarrow 2Fe(OH)_3 + 6NH_4Cl$$
$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O.$$

From these equations it is seen that one molecular weight in grams (one *mole*) of $FeCO_3$ will furnish one molecular weight in grams of $FeCl_2$, or two moles of $FeCO_3$ will furnish two moles of $FeCl_2$. Two moles of $FeCl_2$ will give two moles of $FeCl_3$, which in turn will precipitate two moles of $Fe(OH)_3$ and this last compound on ignition will give *one* mole of Fe_2O_3. Hence every two moles (231.69 grams) of $FeCO_3$ will eventually furnish one mole (159.68 grams) of Fe_2O_3, and it will do so independently of the nature of the process or composition of the reagents used to bring about the conversion. Indeed, the above reactions are better written in the ionic form, thus:

$$FeCO_3 + 2H^+ \rightarrow Fe^{++} + CO_2 + H_2O$$
$$Fe^{++} + \oplus \rightarrow Fe^{+++}$$
$$Fe^{+++} + 3OH^- \rightarrow Fe(OH)_3$$
$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O.$$

and for purposes of calculations all the intermediate steps may be omitted and the fundamental change expressed by the hypothetical equation:

$$2FeCO_3 + O \rightarrow Fe_2O_3 + 2CO_2.$$

In general the student will find it unnecessary to determine the weights of intermediate products in a reaction which takes place in steps, and for purposes of calculation need consider only the initial and final substances.

It has been shown that two moles (231.69 grams) of $FeCO_3$ will furnish one mole (159.68 grams) of Fe_2O_3. By simple proportion, one *gram* of Fe_2O_3 will be obtained from $1 \times \frac{2FeCO_3}{Fe_2O_3} = 1 \times \frac{231.69}{159.68} = 1.4510$ grams of $FeCO_3$, and since each mole of $FeCO_3$ contains one gram-atomic weight (55.84 grams) of Fe and represents the equivalent of one mole (71.84 grams) of FeO ($FeCO_3 \rightarrow FeO + CO_2$), the corresponding weights of Fe and FeO would be $1 \times \frac{2Fe}{Fe_2O_3} = 1 \times \frac{2 \times 55.84}{159.68} = 0.6994$ gram of Fe, and $1 \times \frac{2FeO}{Fe_2O_3} = 1 \times \frac{2 \times 71.84}{159.68} = 0.8998$ gram of FeO respectively. *Ans.*

EXAMPLE II.—What weight of Fe_3O_4 will furnish 1.000 gram of Fe_2O_3?

Whatever equations may be written to represent the conversion of the Fe_3O_4 to the Fe_2O_3 it will be found that from every two moles of Fe_3O_4 there are obtained three moles of Fe_2O_3, and the hypothetical equation may be written:

$$2Fe_3O_4 + O \rightarrow 3Fe_2O_3.$$

Hence, $1.000 \times \frac{2Fe_3O_4}{3Fe_2O_3} = 1.000 \times \frac{463.0}{479.0} = 0.9668$ gram Fe_3O_4. *Ans.*

17. Chemical Factors.—A chemical factor may be defined as the weight of desired substance contained in, obtainable from, or equivalent to a unit weight of given substance. Thus, in the above three examples, the numbers obtained from the ratios $\frac{Cl}{AgCl}$, $\frac{2FeCO_3}{Fe_2O_3}$, $\frac{2Fe}{Fe_2O_3}$, $\frac{2FeO}{Fe_2O_3}$, and $\frac{2Fe_3O_4}{3Fe_2O_3}$ are chemical factors

since they represent the respective weights of Cl, $FeCO_3$, Fe, FeO and Fe_3O_4 contained in, obtained from, or equivalent to one unit weight of AgCl or of Fe_2O_3 as the case may be.

A weight of one substance is said to be *equivalent* to that of another substance when the two will mutually enter into direct or indirect reaction in exact respective proportion to those weights. In the example cited above, 231.69 grams of $FeCO_3$ produce 159.68 grams of Fe_2O_3. Hence 231.69 grams of $FeCO_3$ are equivalent to 159.68 grams of Fe_2O_3. The equivalent weights of elements and compounds may be expressed by mutual proportions as in the case just given, or they may be referred to a common standard for which purpose the atomic weight of hydrogen (1.008) is usually taken. According to this system, the equivalent weight of an element or compound is that weight of it which will involve in active reaction one atomic weight of hydrogen or a weight of any other substance which in turn will involve in reaction one atomic weight of hydrogen.

It is important to notice that in expressing a chemical factor the atomic or molecular weight of the substance *sought* is placed in the numerator, the atomic or molecular weight of the substance *weighed* is placed in the denominator, and the coefficients are adjusted *in accordance with the reactions involved.* When the principal element or radical desired occurs in both numerator and denominator, usually the number of atomic weights of this element or radical will be the same in both numerator and denominator, although there are instances when this is not true. For example, in the reaction

$$2CuCl \rightarrow CuCl_2 + Cu,$$

the weight of free copper liberated from one gram of cuprous chloride is $1 \times \frac{Cu}{2CuCl}$, $= 0.3210$ gram, and 0.3210 is the chemical factor in this particular case.

That the principal element does not always occur in both numerator and denominator is shown in the determination of bromine by precipitation as silver bromide and conversion to silver chloride with a current of chlorine:

$$2AgBr + Cl_2 \rightarrow 2AgCl + Br_2.$$

Here the weight of bromine represented by one gram of silver chloride is $\frac{Br_2}{2AgCl}' = \frac{2 \times 79.92}{2 \times 143.34}' = 0.5578$ gram.

Problems

37. Calculate by logarithms the following factors:

$$(a)\ \frac{S}{BaSO_4};\ (b)\ \frac{Ba}{BaSO_4};\ (c)\ \frac{2Al}{Al_2O_3};\ (d)\ \frac{Na_2O}{2NaCl}$$

Ans. (*a*) 0.1373; (*b*) 0.5885; (*c*) 0.529; (*d*) 0.5303.

38. Balance by common constituent and calculate the following factors:

$$(a)\ \frac{CN}{AgCN};\ (b)\ \frac{B}{B_2O_3};\ (c)\ \frac{NH_4}{(NH_4)_2PtCl_6};\ (d)\ \frac{Cr}{Cr_2O_3}.$$

Ans. (*a*) 0.1943; (*b*) 0.312; (*c*) 0.08126; (*d*) 0.684.

39. Balance by common constituent and calculate the log factors for the following:

$$(a)\ \frac{Ag_2O}{AgCl};\ (b)\ \frac{FeS_2}{BaSO_4};\ (c)\ \frac{N_2}{C_{20}H_{17}N_5O_3};\ (d)\ \frac{P}{(NH_4)_3PO_4 \cdot 12MoO_3}$$

Ans. (*a*) 9.9076 − 10; (*b*) 9.4100 − 10; (*c*) 9.2710 − 10; (*d*) 8.2184 − 10.

40. Calculate the chemical factors of the following:

Weighed	Sought
(*a*) $(NH_4)_2PtCl_6$	N
(*b*) Cu_2S	CuO
(*c*) AgCl	$NaClO_4$
(*d*) K_2PtCl_6	K
(*e*) K_2PtCl_6	K_2O

Ans. (*a*) 0.06310; (*b*) 0.9995; (*c*) 0.8549; (*d*) 0.1608; (*e*) 0.1937.

41. Calculate the log chemical factor for each of the following:

Weighed	Sought
(*a*) ferric oxide	iron
(*b*) ferric oxide	ferrous oxide
(*c*) water	hydrogen
(*d*) cupric oxide	copper
(*e*) barium sulphate	sulphuric acid
(*f*) calcium carbonate	carbon dioxide

Ans. (*a*) 9.8446 − 10; (*b*) 9.9541 − 10; (*c*) 9.0487 − 10; (*d*) 9.9025 − 10; (*e*) 9.6235 − 10; (*f*) 9.6432 − 10.

42. Calculate the chemical factors for (*a*) Sn in SnO_2; (*b*) Pb in $PbCrO_4$ (*c*) Pb in PbO_2; (*d*) Pb in $PbSO_4$; (*e*) Pb in $PbCl_2$.

Ans. (*a*) 0.7877; (*b*) 0.6411; (*c*) 0.8662; (*d*) 0.6832; (*e*) 0.7450

43. Calculate the chemical factors for the following:

Weighed	Sought	With Reference to
(*a*) Ag	Br	AgBr
(*b*) Ag	HCl	AgCl
(*c*) Fe_2O_3	SO_3	$FeSO_4$
(*d*) Pt	K	K_2PtCl_6
(*e*) AgCl	I	AgI
(*f*) Pt	KCl	K_2PtCl_3
(*g*) Pt	NH_3	$(NH_4)_2PtCl_6$

Ans. (*a*) 0.7407; (*b*) 0.3379; (*c*) 1.003; (*d*) 0.4006; (*e*) 0.8856; (*f*) 0.7639; (*g*) 0.1746.

44. Calculate the chemical factors for (*a*) $(NH_4)_2O$ from $(NH_4)_2PtCl_6$; (*b*) Fe_2O_3 from Fe_3O_4; (*c*) ZnO from $ZnNH_4PO_4.2H_2O$; (*d*) As_2O_3 from $Cu_3(AsO_3)_2.2AsO_3.Cu(C_2H_3O_2)_2$; (*e*) As_2O_5 from $PbHAsO_4$; (*f*) $Ba_3(PO_4)_2$ from $BaSO_4$; (*g*) PbO from $Pb_3(AsO_4)_2$; (*h*) $PbCrO_4$ from Cr_2O_3.

Ans. (*a*) 0.1173; (*b*) 1.035; (*c*) 0.3794; (*d*) 0.4580; (*e*) 0.3311; (*f*) 0.8596; (*g*) 0.7443; (*h*) 4.243.

18. Application of Chemical Factors to Percentage Computations.—Since the chemical factor represents the weight of desired element or compound equivalent to one *unit* weight of the element or compound weighed, from any weight of the latter the weight of the former may be readily calculated. The percentage of that substance present in the sample may be found by dividing by the weight of sample and multiplying by one hundred.

Example I.—If 2.000 grams of impure sodium chloride are dissolved in water and with an excess of silver nitrate, 4.6280 grams of silver chloride are precipitated, what is the percentage of chlorine in the sample?

The chemical factor of Cl in AgCl is 0.2474, indicating that 1 gram of AgCl contains 0.2474 gram of Cl. In 4.6280 grams of AgCl there are therefore $4.6280 \times 0.2474 = 1.145$ grams of Cl. Since this amount represents the chlorine present in 2.000 grams of the material, the percentage weight of chlorine must be $\frac{1.145}{2.000} \times 100 = 57.25$ per cent. *Ans.*

Example II.—A half-gram sample of impure magnetite (Fe_3O_4) is converted by chemical reactions to Fe_2O_3 weighing 0.4110 gram. What is the percentage of Fe_3O_4 in the magnetite?

The chemical factor of Fe_3O_4 from Fe_2O_3 is $\frac{2Fe_3O_4}{3Fe_2O_3} = 0.9668$ which represents the weight of Fe_3O_4 equivalent to 1 gram of Fe_2O_3. The weight of Fe_3O_4 equivalent to 0.4110 gram of Fe_2O_3

must be $0.4110 \times 0.9668 = 0.3974$ gram, and the percentage of Fe_3O_4 in the sample must be $\frac{0.3974}{0.5000} \times 100 = 79.48$ per cent. *Ans.*

Problems

45. What is the weight of sulphur in 5.672 grams of barium sulphate?

Ans. 0.7790 gram.

46. A material containing a soluble lead salt gave a precipitate with sulphuric acid weighing 0.1672 gram. To what weight of (*a*) Pb; (*b*) $PbCl_2$; (*c*) PbS; (*d*) $PbCO_3$ does this correspond?

Ans. (*a*) 0.1142 gram; (*b*) 0.1533 gram; (*c*) 0.1319 gram; (*d*) 0.1473 gram.

47. Calculate the weight of anhydrous $Ca(NO_3)_2$ which must be heated in order to obtain the following weights of CaO: (*a*) 0.624 gram; (*b*) 0.964 lb.; (*c*) 0.2463 ton; (*d*) 0.2172 oz.

Ans. (*a*) 1.83 grams; (*b*) 2.821 lbs.; (*c*) 0.7207 ton; (*d*) 0.6357 oz.

48. How much pure silver must be dissolved in HNO_3 to give 300.0 grams of $AgNO_3$?

Ans. 190.5 grams.

49. What is the weight of the constituent elements in 0.7170 gram of $AgNO_3$?

Ans. Ag = 0.4553 gram; N = 0.0591 gram; O = 0.2026 gram.

50. How many pounds of pure CaO can be made from 96.0 pounds of pure $CaCO_3$?

Ans. 53.8 lbs.

51. Calculate the pounds of materials theoretically necessary for the preparation of one pound of (*a*) KOH from CaO and K_2CO_3; (*b*) $BaSO_4$ from $Na_2SO_4.10H_2O$ and $BaCl_2.2H_2O$.

Ans. (*a*) CaO = 0.4997 lb.; K_2CO_3 = 1.230 lbs.

(*b*) $Na_2SO_4.10H_2O$ = 1.380 lbs.; $BaCl_2.2H_2O$ = 1.044 lbs.

52. A piece of silver dime weighing 0.2000 gram is dissolved and with an excess sodium chloride gives a precipitate of silver chloride weighing 0.2393 gram. What is the percentage of silver in the dime?

Ans. 90.10 per cent.

53. A sample of impure ferrous ammonium sulphate weighs 0.5013 gram and furnishes 0.0968 gram of Fe_2O_3. What is the percentage of $Fe(NH_4)_2(SO_4)_2.6H_2O$?

Ans. 94.82 per cent.

54. A sample of limestone weighing 1.2456 grams furnishes 0.0228 gram of Fe_2O_3, 1.3101 grams of $CaSO_4$, and 0.0551 gram of $Mg_2P_2O_7$. Calculate the percentage of (*a*) Fe; (*b*) CaO; (*c*) MgO in the limestone. What weight of CO_2 could be in combination with the calcium?

Ans. (*a*) 1.28 per cent; (*b*) 43.32 per cent; (*c*) 1.60 per cent. 0.4237 gram.

55. What weight of pyrite containing 36.40 per cent of sulphur must have been taken for analysis in order to give a precipitate of barium sulphate weighing 1.0206 grams?

Ans. 0.3850 gram.

56. What is the percentage composition of a brass containing only copper, lead, and zinc if a half-gram sample furnishes 0.0023 gram of $PbSO_4$ and 0.4108 gram of $ZnNH_4PO_4$? What weight of $Zn_2P_2O_7$ could be obtained by igniting the zinc ammonium phosphate?

Cu = 69.60 per cent
Pb = 0.31 per cent
Zn = 30.09 per cent

Ans. 0.3510 gram.

57. How many ounces of (*a*) NaOH; (*b*) KOH; (*c*) Na_2CO_3; (*d*) $KNaCO_3$ will be neutralized by 1 pound of $KHSO_4$?

Ans. (*a*) 4.702 oz.; (*b*) 6.593 oz.; (*c*) 6.227 oz.; (*d*) 7.173 oz.

58. How many grams of NaOH are equivalent to the Na in the NaCl required to precipitate AgCl from two grams of $AgNO_3$?

Ans. 0.4710 gram.

19. Gravimetric Problems Involving a Factor Weight Sample.—It is often desirable in industrial work where a large number of samples of similar material are analyzed to regulate the weight of sample so that the weight of the final product obtained multiplied by a simple factor shall exactly equal the percentage of the desired constituent. This makes it possible to have the sample weighed out directly against a tare, perhaps by some one inexperienced in exact weighing, and at the same time to eliminate both the tedious calculations necessary for each analysis and the possibility of mathematical errors.

The calculation of a chemical analysis involving a direct gravimetric determination is carried out by means of the following formula:

$$\frac{\text{weight of product} \times \text{chemical factor}}{\text{weight of sample}} \times 100 = \text{per cent of desired constituent.}$$

Since for a specific determination the chemical factor is a constant, the expression contains only three variable factors, namely, the weight of product, the weight of sample, and the percentage of desired constituent. If any two are known, the third can be calculated; or since the expression involves only multiplication and division, if the numerical *ratio* between the weight of product and the weight of sample, or between the weight of product and the percentage of desired constituent, is known, the remaining term can be determined. Thus, if the weight of product is numerically *equal* to the percentage of desired

constituent, these values cancel, and the weight of sample becomes equal to one hundred times the chemical factor. If the weight of product is numerically *equal* to the weight of sample, these values cancel, and the percentage of desired constituent becomes equal to one hundred times the chemical factor. Other ratios may be inserted in the expression and the calculation made in a similar way.

EXAMPLE I.—The chemical factor of a certain analysis is 0.3427. It is desired to regulate the weight of sample taken so that each centigram of the precipitate obtained shall represent 1 per cent of the desired constituent.

From the data, the relation between the weight of precipitate and the percentage of desired constituent is fixed so that 0.01 gram $\doteq$ 1 per cent. Hence the solution of the problem involves only substitution:

$$0.3427 \times 0.01 \times \frac{100}{x} = 1$$

$$x = 0.3427 \text{ gram.} \quad \textit{Ans.}$$

Similarly, if the problem reads "so that the number of centigrams of precipitate obtained shall represent the percentage of desired constituent," the expression is exactly the same, and the weight of sample is, as above, 0.3427 gram.

EXAMPLE II.—The chemical factor of a certain analysis is 0.3427. It is desired to regulate the weight of sample taken so that every 2 centigrams of precipitate obtained shall represent 1 per cent of the desired constituent.

The ratio between the weight of precipitate and the percentage of desired constituent is so fixed that 0.02 gram $\doteq$ 1 per cent, and the problem involves only substitution:

$$0.3427 \times 0.02 \times \frac{100}{x} = 1$$

$$x = 0.6854 \text{ gram.} \quad \textit{Ans.}$$

On the other hand, if the problem reads "so that twice the number of centigrams of precipitate obtained shall represent the percentage of desired constituent," the number of centigrams must be multiplied by 2 in order to become equal to the percentage. Hence, the expression for substitution becomes $\frac{0.01}{2}$

gram $\simeq$ 1 per cent, where it is seen that the above condition is fulfilled.

$$0.3427 \times \frac{0.01}{2} \times \frac{100}{x} = 1$$

$$x = 0.1714 \text{ gram.} \quad \textit{Ans.}$$

EXAMPLE III.—The chemical factor of a certain analysis is 0.3427. It is desired to regulate the weight of sample so that three-fourths of the weight in grams of the precipitate obtained shall equal one-fiftieth of the percentage of desired constituent.

It is only necessary to substitute in the expression such numerical values for the weight of precipitate and the percentage of constituent that three-fourths of the former shall equal one-fiftieth of the latter. This is most simply done by taking the respective reciprocals of the given ratios, thus:

$$\frac{4}{3} \text{ gram} \simeq 50 \text{ per cent,}$$

where it is seen that the condition is fulfilled.

Substituting and solving,

$$0.3427 \times \frac{4}{3} \times \frac{100}{x} = 50$$

$$x = 0.9135 \text{ gram.} \quad \textit{Ans.}$$

Problems

59. In the analysis of a sample of feldspar for silica, the sample is fused, dissolved in HCl, and the solution is evaporated to dryness, heated, and treated with acid. The residue is filtered off and weighed as SiO_2. What weight of sample should be taken for analysis so that (*a*) each centigram of residue shall represent 1 per cent SiO_2; (*b*) the number of centigrams shall represent directly the percentage SiO_2; (*c*) every 2 centigrams of residue shall represent 1 per cent SiO_2; (*d*) twice the number of centigrams shall equal the percentage of SiO_2?

Ans. (*a*) 1.00 gram; (*b*) 1.00 gram; (*c*) 2.00 grams; (*d*) 0.500 gram.

60. In the analysis of a sample of lead salt, the lead is determined as $PbSO_4$. What weight of sample should be taken for analysis such that the weight of lead sulphate in grams obtained shall represent (*a*) one-thirtieth the percentage of lead in the sample expressed as Pb; (*b*) one-thirtieth the percentage of lead expressed as PbO_2; (*c*) one-thirtieth the percentage of lead expressed as $PbCrO_4$?

Ans. (*a*) 2.277 grams; (*b*) 2.629 grams; (*c*) 3.553 grams.

61. A sample of ammonium salt is analyzed by precipitating the ammonium radical as $(NH_4)_2PtCl_6$ and igniting the precipitate to metallic platinum. Calculate the weight of sample to be taken for analysis (*a*) so that

the weight of ignited precipitate in grams multiplied by the atomic weight of platinum shall give the per cent N in the sample; (*b*) so that the weight of ignited precipitate in milligrams multiplied by $\frac{3}{100}$ shall equal four-thirds of the per cent NH_3 in the sample.

Ans. 0.07357 gram; (*b*) 0.7753 gram.

62. What weight of dolomite should be taken for analysis so that the per cent Mg is found by multiplying by 50 the weight in grams of $Mg_2P_2O_7$ obtained?

Ans. 0.4368 gram.

63. What weight of substance containing iron should be taken for analysis so that each milligram of ignited Fe_2O_3 corresponds to 0.1 per cent FeO in the sample?

Ans. 0.8998 gram.

64. What weight of cast iron should be taken for analysis so that the weight of ignited SiO_2 in centigrams will be equal to one-third of the per cent Si in the cast iron?

Ans. 0.156 gram.

65. What weight of pyrite should be taken for analysis such that 1 gram of $BaSO_4$ will be obtained for each 40 per cent sulphur in the sample?

Ans. 0.3433 gram.

66. Calculate the weight of limestone to be taken so that the centigrams of CaO obtained and the percentage of Ca in the sample shall be in the respective ratio of 7 to 5.

Ans. 1.001 grams.

20. Calculation of the Volume of a Reagent Required for a Given Reaction.—The volume of a solution required to carry out a given reaction may be calculated by gravimetric methods if the quantitative composition of the solution is definitely known. This composition may be expressed as the weight of solute contained in a unit volume of solution or in such a way that the weight of solute per unit volume can be directly determined. Thus, the concentration of the solution may be expressed in terms of the number of moles (molecular weight in grams) of solute or the number of equivalents (discussed in detail in Chap. VIII) of solute in a given volume. Likewise, if the percentage-by-weight composition of the reagent and its specific gravity are known, the weight of solute in a unit volume of solution may be found. In all these cases, the volume of the solution required for a given reaction can be calculated. The principles involved are the same as those outlined in the preceding sections. The weight of the reactive component of the required reagent is determined by means of the weight of the substance reacted upon and the chemical factor. This weight, divided by the

weight of the solute per unit volume of solution, will give the volume of solution required for the reaction.

When the strength of the reagent is given in terms of grams per liter, the determination is very simple.

EXAMPLE I.—How many cubic centimeters of barium chloride solution containing 90.0 grams of $BaCl_2.2H_2O$ per liter are required to precipitate the sulphate as $BaSO_4$ from 10.0 grams of pure $Na_2SO_4.10H_2O$?

The weight of $BaCl_2.2H_2O$ for the precipitation is found by means of the chemical factor, thus,

$$10.0 \times \frac{BaCl_2.2H_2O}{Na_2SO_4.10H_2O} = 10.0 \times \frac{244}{322} = 7.58 \text{ grams of } BaCl_2.2H_2O.$$

Since each cubic centimeter of reagent contains 0.0900 gram of $BaCl_2.2H_2O$, the volume of solution required is

$$\frac{7.58}{0.0900} = 84.2 \text{ c.c.} \quad Ans.$$

When the concentration of the required reagent is expressed in terms of the percentage by weight of the solute, the specific gravity of the solution must also be known in order to determine the volume required. There is no exact mathematical relationship between these two factors, but tables are given in all standard chemical handbooks showing this relationship for solutions of common substances experimentally determined at many different concentrations. Consequently, when a problem includes only one of these factors, tables must be consulted in order to determine the other. In the appendix of this book specific gravity percentage tables are given for a few common acids and bases.

EXAMPLE II.—How many cubic centimeters of ammonia water of specific gravity 0.950 (containing 12.72 per cent of NH_3 by weight) are required to precipitate the iron from 0.8000 gram of pure ferrous ammonium sulphate, $FeSO_4.(NH_4)_2SO_4.6H_2O$, after oxidation of the iron to the ferric state?

Since three molecules of ammonia are required to precipitate one atom of ferric iron:

$$Fe^{+++} + 3NH_3 + 3H_2O \rightarrow Fe(OH)_3 + 3NH_4^+,$$

it follows that the weight of NH_3 necessary to precipitate the

iron from 0.8000 gram of ferrous ammonium sulphate will be

$$0.8000 \times \frac{3NH_3}{FeSO_4.(NH_4)_2SO_4.6H_2O} = 0.8000 \times \frac{51.10}{392.1} =$$

0.1043 gram of NH_3.

Since the ammonia water has a specific gravity of 0.950 and contains 12.74 per cent of NH_3 by weight, 1 c.c. of the solution weighs 0.950 gram of which 12.74 per cent by weight is NH_3 and 87.26 yer cent by weight is water. The actual weight of NH_3 in 1 c.c. of solution is therefore $0.950 \times 0.1274 = 0.121$ gram. Since 0.1043 gram of NH_3 is required to precipitate the iron and since each cubic centimeter of the solution contains 0.121 gram of NH_3, it follows that the volume of solution required is

$$\frac{0.1043}{0.121} = 0.862 \text{ c.c.} \quad \textit{Ans.}$$

As explained in Sec. 16, in calculations of this type, the computations should not be carried through unnecessary steps. In the example above, it is not necessary to compute the weight of iron contained in the ferrous ammonium sulphate, the weight of ammonium hydroxide required to precipitate the iron, and the weight of anhydrous ammonia contained in the ammonium hydroxide. On expressing the whole, the common factors cancel:

$$0.8000 \times \frac{(Fe)^*}{FeSO_4.(NH_4)_2SO_4.6H_2O} \times \frac{(3NH_4OH)^*}{(Fe)^*} \times \frac{3NH_3}{(3NH_4OH)^*} = 0.1043 \text{ gram of } NH_3.$$

$$\frac{0.1043}{0.121} = 0.862 \text{ c.c. as above.}$$

In general, with problems of this type time will be saved if the final multiplications and divisions are not made until all the factors are combined and expressed as a whole. In the above example the only essential factors are

$$\frac{0.8000 \times 51.10}{392.1 \times 0.950 \times 0.1274} = 0.862 \text{ c.c.} \quad \textit{Ans.}$$

A very similar type of problem is one in which it is required to calculate the volume of a solution of given percentage composition required to react with a certain volume of another solution of given percentage composition. By computing the weight

of reacting component in the given volume of the latter solution, the problem becomes exactly like the one discussed above.

EXAMPLE III.—How many cubic centimeters of hydrochloric acid (sp. gr. 1.140, containing 27.66 per cent HCl by weight) are required to neutralize 75.0 c.c. of ammonium hydroxide (sp. gr. 0.960 containing 9.91 per cent NH_3 by weight)?

In 75.0 c.c. of the ammonia solution there are

$$75.0 \times 0.960 \times 0.0991 \text{ grams of } NH_3.$$

The required weight of HCl for this NH_3 is

$$75.0 \times 0.960 \times 0.0991 \times \frac{HCl}{NH_3} =$$

$$75.0 \times 0.960 \times 0.0991 \times \frac{36.46}{17.02} \text{ grams.}$$

Since each cubic centimeter of the acid contains 1.140×0.2766 gram of HCl, the volume of acid required is

$$\frac{75.0 \times 0.960 \times 0.0991 \times 36.46}{1.140 \times 0.2766 \times 17.02} = 48.5 \text{ c.c.} \quad \textit{Ans.}$$

Problems

67. It is desired to precipitate completely the silver from a solution which contains 0.250 gram of silver. How many cubic centimeters of ammonium chloride solution (53.6 grams of NH_4Cl per liter) will be required?

Ans. 2.31 c.c.

68. How many cubic centimeters of bromine water containing 30 grams of Br_2 per liter will be required to oxidize the iron in 2.176 grams of pure $FeSO_4.7H_2O$ in the presence of acid? ($2Fe^{++} + Br_2 \rightarrow 2Fe^{+++} + 2Br^-$).

Ans. 20.9 c.c.

69. What volume of ammonium oxalate solution (35.1 grams of $(NH_4)_2C_2O_4.H_2O$ per liter) will be required to precipitate the calcium as CaC_2O_4 from 0.1242 gram of apatite ($Ca_3(PO_4)_2.CaCl_2$)? What volume of "magnesia mixture" containing one mole (molecular weight in grams) of $MgCl_2$ per liter will be necessary to precipitate the phosphate as $MgNH_4PO_4$ from the filtrate from the calcium determination?

Ans. 4.77 c.c.; 0.59 c.c.

70. In the precipitation of arsenic as $MgNH_4AsO_4$ from a solution of 0.4000 gram of pure As_2O_3 which has been oxidized to arsenic acid, it is desired to add sufficient magnesium chloride reagent (64 grams $MgCl_2$ per liter) to precipitate the arsenic and also have 0.2 gram of Mg remaining in solution. What volume is required?

Ans. 18.26 c.c.

71. Chloride samples are to be prepared for student analysis by using the chlorides of sodium, potassium, and ammonium, alone or mixed in various

proportions. How many cubic centimeters of 5 per cent silver nitrate (*i.e.*, containing 5 grams $AgNO_3$ in 100 grams of solution) of specific gravity 1.041 must be added to a 0.300-gram sample in order to insure complete precipitation in every possible case?

Ans. 18.3 c.c.

72. Given a solution of nitric acid (sp. gr. 1.200, containing 32.36 per cent HNO_3 by weight). How many grams of HNO_3 are contained in 1 c.c. of the solution?

Ans. 0.3884 gram.

73. Calculate the weight of HNO_3 in (*a*) 10 c.c. of nitric acid, sp. gr. 1.230, containing 36.78 per cent HNO_3 by weight; (*b*) 9.50 c.c. of nitric acid, sp. gr. 1.150; (*c*) 21.2 c.c. of nitric acid, sp. gr. 1.473.

Ans. (*a*) 4.525 grams; (*b*) 2.71 grams; (*c*) 26.17 grams.

74. How many cubic centimeters of aqueous ammonia (sp. gr. 0.900) are required to precipitate the iron as $Fe(OH)_3$ from a half-gram sample of pure $Fe_2(SO_4)_3.9H_2O$?

Ans. 0.36 c.c.

75. Calculate the volume of hydrochloric acid (sp. gr. 1.050, containing 10.17 per cent HCl by weight) to neutralize (*a*) 48.6 c.c. of a solution of KOH (sp. gr. 1.100 containing 12.0 per cent KOH by weight); (*b*) 152.1 c.c. of a solution of NaOH (sp. gr. 1.327); (*c*) a solution containing 10 grams of pure KOH; (*d*) a solution containing 10 grams of impure KOH (96.6 per cent KOH, 2.2 per cent K_2CO_3, 1.2 per cent H_2O); (*e*) 25.3 c.c. of ammonia water containing 15.04 per cent by weight of NH_3.

Ans. (*a*) 39.0 c.c.; (*b*) 508 c.c.; (*c*) 60.87 c.c.; (*d*) 59.8 c.c.; (*e*) 80.0 c.c.

76. The following are added to water: 1.60 grams of pure Na_2CO_3, 2.21 c.c. of H_2SO_4 solution (sp. gr. 1.700), and 16.0 c.c. of KOH solution (56 grams of solid per liter). This solution is to be brought to the exact neutral point. The solutions available for this purpose are hydrochloric acid (sp. gr. 1.141) and ammonia water (sp. gr. 0.930). Which should be used? What volume is required?

Ans. 1.26 c.c. of ammonia water.

77. In the reaction $2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$ it is desired to add sufficient sulphuric acid (sp. gr. 1.835) to liberate that amount of HCl which when absorbed in water will furnish 250 c.c. of solution of specific gravity 1.040. Calculate the volume necessary.

Ans. 16.7 c.c.

21. Indirect Analyses.—There are many types of indirect analyses in analytical chemistry of which some pertain to Gravimetric Analysis, some to Volumetric Analysis, and some to a combination of the two. Problems relating to indirect analyses differ from those of direct analyses in much the same way that algebraic equations involving two or more unknown quantities differ from those involving only one unknown quantity. Indeed, such indirect problems are often solved by algebraic methods.

The simplest type of indirect problem is that in which two pure chemical substances are isolated and weighed together. Then either by further chemical action on the substances or by chemical analysis of a new sample of the same material, additional data are derived by which one of the components is determined. The other component is then found by difference.

EXAMPLE I.—In the analysis of a 2-gram sample of limestone, the weight of combined oxides of iron and aluminum ($Fe_2O_3 + Al_2O_3$) is found to be 0.0812 gram. By volumetric methods, the percentage of total iron calculated as FeO is found to be 1.50 per cent. What is the percentage of Al_2O_3 in the sample?

$$\text{Weight of FeO} = 2.00 \times \frac{1.50}{100} = 0.0300 \text{ gram.}$$

$$\text{Weight of } Fe_2O_3 = 0.0300 \times \frac{Fe_2O_3}{2FeO} = 0.0333 \text{ gram.}$$

$$\text{Weight of } Al_2O_3 = 0.0812 - 0.0333 = 0.0479 \text{ gram.}$$

$$\text{Percentage of } Al_2O_3 = \frac{0.0479}{2.00} \times 100 = 2.40 \text{ per cent.} \quad \textit{Ans.}$$

A second general type of indirect analysis is that in which two chemical substances are isolated and weighed together. Then another measure of the two substances is obtained either by converting them to two different compounds and again finding the combined weights, or by determining the amount of reagent required to effect such conversion. In this way, using algebraic symbols to represent the unknown quantities, two independent equations may be formulated, and from them the values of the unknowns may be determined. For the sake of precision it is advisable to solve simultaneously by cross-multiplying the respective coefficients of the unknowns, for in this way larger coefficients for the symbols are obtained. It is evident that this type of problem may be extended to any number of unknown quantities, provided sufficient data are given to allow the formulation of as many algebraic equations as there are unknowns.

EXAMPLE II.—In the analysis of a 0.5000-gram sample of feldspar, a mixture of the chlorides of sodium and potassium is obtained which weighs 0.1180 gram. Subsequent treatment

with silver nitrate furnishes 0.2451 gram of silver chloride. What is the percentage of Na_2O and of K_2O in the sample?

Let x = weight of KCl,
and y = weight of NaCl.
Then (1) $x + y = 0.1180$.

Number of grams of AgCl obtainable from x grams of KCl

$$= x\left(\frac{\text{AgCl}}{\text{KCl}}\right)$$
$$= 1.923x.$$

Number of grams of AgCl obtainable from y grams of NaCl

$$= y\left(\frac{\text{AgCl}}{\text{NaCl}}\right)$$
$$= 2.452y.$$

Therefore, (2) $1.923x + 2.452y = 0.2451$.

Solving (1) and (2) simultaneously,

$x = 0.0837$ gram of KCl
$y = 0.0343$ gram of NaCl

$$\text{Per cent } K_2O = \left(\frac{K_2O}{2KCl}\right)\frac{0.0837 \times 100}{0.500} = 10.6. \quad \textit{Ans.}$$

$$\text{Per cent } Na_2O = \left(\frac{Na_2O}{2NaCl}\right)\frac{0.0343 \times 100}{0.500} = 3.64. \quad \textit{Ans.}$$

Problems

78. In the analysis of a sample of feldspar weighing 1.060 grams, a mixture of the chlorides of sodium and potassium is obtained which weighs 0.2137 gram. Subsequent treatment converts the potassium into K_2PtCl_6, weighing 0.4910 gram. What is the percentage of Na_2O in the sample?

Ans. 3.19 per cent.

79. A mixture of 0.2600 gram of ferric oxide and 0.4500 gram of aluminum oxide is ignited in hydrogen, the ferric oxide alone being reduced to metallic iron. What is the final weight?

Ans. 0.6318 gram.

80. A silicate weighing 0.6000 gram yields a mixture of pure NaCl and pure KCl weighing 0.1800 gram. In this residue the KCl is converted to K_2PtCl_6 weighing 0.2700 gram. Find the per cent K_2O and the per cent Na_2O in the silicate.

Ans. 8.72 per cent K_2O; 8.60 per cent Na_2O.

81. In the analysis of a sample of feldspar weighing 0.7500 gram there is obtained 0.2200 gram of NaCl + KCl. These chlorides are dissolved in water and treated with chloroplatinic acid. The precipitate of K_2PtCl_6 after treatment with alcohol is filtered on a Gooch crucible, dried, and ignited

in hydrogen; after washing with hot water, the residual platinum then weighs 0.0950 gram. Compute the percentages of Na_2O and K_2O in the feldspar.

Ans. 10.42 per cent Na_2O; 6.11 per cent K_2O.

82. A mixture of silver chloride and silver bromide is found to contain 66.35 per cent of silver. What is the percentage of bromine?

Ans. 21.3 per cent.

83. A mixture of silver chloride and silver bromide weighs 0.5267 gram. By treatment with chlorine, the silver bromide is converted into silver chloride, and the total weight of silver chloride becomes 0.4269 gram. What is the weight of bromine in the original mixture?

Ans. 0.179 gram.

84. A mixture of pure CaO and pure BaO weighing 0.6411 gram yields 1.1201 grams of pure mixed sulphates. Find the percentage of Ba and of Ca in the original mixture.

Ans. 17.6 per cent Ca; 67.4 per cent Ba.

85. A sample of silicate weighing 0.6000 gram yields 0.1803 gram of a mixture of pure NaCl and pure KCl. When these are dissolved and treated with $AgNO_3$, the resulting precipitate of AgCl is found to weigh 0.3904 gram. Calculate the per cent Na_2O and the per cent K_2O.

Ans. 7.32 per cent Na_2O; 10.27 per cent K_2O.

86. From a sample of feldspar a mixture of KCl and NaCl is obtained which weighs 0.1506 gram and contains 55.00 per cent chlorine. What weight of K_2PtCl_6 could be obtained from the KCl?

Ans. 0.212 gram.

87. A mixture of $BaCl_2.2H_2O$ and LiCl weighs 0.6000 gram, and with silver nitrate solution yields 1.440 grams of AgCl. Calculate the per cent Ba in the original mixture.

Ans. 25.0 per cent.

88. A mixture of pure NaCl and pure NaI weighs 0.4000 gram and yields with $AgNO_3$ a precipitate of AgCl and AgI which weighs 0.8981 gram. Find the per cent iodine present in the original mixture.

Ans. 19.8 per cent.

89. What percentage of $MgCO_3$ is present with pure $BaCO_3$ so that the mixture contains the same CO_2 content as if it were pure $CaCO_3$?

Ans. 72.5 per cent.

22. Calculation of Atomic Weights.—It is assumed that the student is already familiar with the principles underlying the determination of the atomic weights of the elements, but for purposes of review, these principles are outlined below.

1. The atomic weight of an element is the weight of its atom as compared to the weight of an atom of oxygen, which, for convenience, is given the value 16.

2. Since the atoms themselves cannot be weighed, indirect methods must be used to determine the atomic weight of an element.

3. In ordinary chemical reactions, the atoms are indivisible and must react as units. The molecule of a chemical compound therefore contains whole numbers of atoms of each elementary constituent.

4. The number of unit weights of an element which will exactly combine with 16 unit weights of oxygen, or with an amount of some other element which in turn will combine with 16 unit weights of oxygen, represents either the atomic weight of the given element or a simple multiple or sub multiple of it.

5. The atomic weight is obtained by determining which multiple or sub multiple of the combining weight it is. Since only an approximate determination is necessary to establish this multiple, any one of the following principles may be used for the purpose:

(*a*) The gram-atomic weight (atomic weight in grams) of an element may be taken as the smallest of the weights of the element found in 22.4 liters (the gram-molecular volume) of all its volatile compounds when measured under standard conditions. In case there are no volatile compounds, other methods may sometimes be used to determine the molecular weights of the compounds, for example, the raising of boiling points and the lowering of freezing points. The value obtained by these methods may possibly still be a multiple of the atomic weight, but in the absence of further data and for all practical purposes, this value is as serviceable as the true atomic weight would be.

(*b*) The physical and chemical properties of the element usually serve to place it in its proper position in the periodic tables, where its approximate atomic weight may be found.

(*c*) The Law of Dulong and Petit states that the atomic weight of an element may, with few exceptions, be fairly approximately determined by dividing the value 6.4 by the specific heat of the element.

These principles are illustrated by the following:

I. A certain element gives a compound with lead which on careful analysis is found to contain 43.548 per cent of the element and 56.452 per cent of lead. Since 207.20 grams of lead will combine with 16 grams of oxygen to form PbO, and since the weight of the element combined with this weight of lead is $43.548 \times \frac{207.20}{56.452} =$

159.84 grams, the value 159.84 or its simple multiple or submultiple must represent the atomic weight of the element.

II. The following compounds of the same element are either gaseous or can be measured in the gaseous state, and the gram-molecular volume contains in each case the approximate weights of the element given below:

	Approximate Weight of Element in 22.4 Liters of Gaseous Compound, Grams
Elementary gas	160
Hydrogen compound	80
Boron compound	240
Methyl compound	80
Ethyl compound	80
Phenyl compound	80
Ethylene compound	160

Apparently the smallest possible weight of the element in the molecular weight of any of its compounds is approximately 80, and the correct atomic weight is therefore $\frac{159.84}{2} = 79.92$. It should be emphasized that since the quantitative measurement of a gas, which in itself cannot follow the gas laws exactly, is of lower degree of accuracy than a carefully made quantitative analysis, it should be used only to show which member of the combining-weight series represents the atomic weight, and should not be used to furnish the atomic weight itself.

III. It is found that 0.084 calorie is required to raise the temperature of 1 gram of the same element 1°C. This is therefore the specific heat of the element, and according to the Law of Dulong and Petit, the approximate atomic weight is $\frac{6.4}{0.084} = 76$. The simple multiple of the combining weight which approximates this value is again $\frac{159.84}{2} = 79.92$. Hence, 79.92 is considered the atomic weight of the element.

Determinations of atomic weight values in the future will be chiefly concerned with revisions of those already established in order that their accuracy may be in keeping with improved apparatus and methods. In such cases, the formulae of the compounds involved are well established and the required calculations are thereby made very simple. The experimental

procedure usually followed is to prepare from the element a known compound of high degree of purity. This compound is weighed and the percentages of its constituents are determined gravimetrically. The mathematical computations involved are exactly similar to those of an ordinary gravimetric analysis, except that the atomic weight of the desired element is the only unknown factor.

EXAMPLE I.—Carefully purified sodium chloride weighing 2.56823 grams furnishes 6.2971 grams of silver chloride. Assuming the atomic weights of the chlorine and silver to be established as 35.46 and 107.88 respectively, calculate the atomic weight of sodium.

$$\text{Weight of NaCl} = \text{weight of AgCl} \times \frac{\text{NaCl}}{\text{AgCl}}$$

$$2.56823 = 6.2971 \times \frac{\text{NaCl}}{\text{AgCl}}$$

$$2.56823 = 6.2971 \times \frac{\text{Na} + 35.46}{107.88 + 35.46}.$$

Solving, Na = 23.00. *Ans.*

Problems

90. If silver phosphate is found by careful analysis to contain 77.300 per cent silver, what is the atomic weight of phosphorus (Ag = 107.88)?

Ans. 31.04.

91. From an average of 13 experiments, Baxter finds the ratio of silver bromide to silver chloride to be 1.310171. Taking the atomic weight of silver as 107.880 and that of chlorine as 35.457, what is the atomic weight of bromine?

Ans. 79.915.

92. The atomic weight of tellurium may be determined by finding the weights of tellurium bromide obtainable from samples of the pure element. From the following values, calculate the average value for the atomic weight of tellurium (Br = 79.92):

	GRAMS OF Te	GRAMS OF $TeBr_4$
1	0.30055	1.05425
2	0.19981	0.70095
3	0.22032	0.77305
4	0.15816	0.55472
5	0.43691	1.53236
6	0.29811	1.04549

Ans. 127.48.

93. In determining the atomic weight of manganese, Berzelius in 1828 obtained 0.7225 gram of Mn_2O_3 from 0.5075 gram of Mn. Von Hauer in

1857 obtained 13.719 grams of Mn_3O_4 from 12.7608 grams of MnO. In 1906, Baxter and Hines obtained an average of 11.43300 grams of AgBr from 6.53738 grams of $MnBr_2$. What are the three values as determined? (Br = 79.916.) Assuming the last value to be correct, what were the percentage errors of the results obtained by Berzelius and Von Hauer?

Ans. 56.66; 55.024; 54.932; 3.15 per cent; 0.166 per cent.

94. In determining the atomic weight of boron, Smith and Van Haagen obtained the data given below and assumed the following atomic weights; O = 16.00; Na = 22.997; Cl = 35.457; S = 32.069; N = 14.010; C = 12.005. Calculate the atomic weight of boron from each result and express the average value of five significant figures. Which figures do you consider uncertain?

(*a*) 0.89853 gram $Na_2B_4O_7$ yielded 0.52112 gram NaCl
(*b*) 0.89853 gram $Na_2B_4O_7$ yielded 0.63313 gram Na_2SO_4
(*c*) 0.69695 gram $Na_2B_4O_7$ yielded 0.49113 gram Na_2SO_4
(*d*) 1.59374 grams $Na_2B_4O_7$ yielded 1.12315 grams Na_2SO_4
(*e*) 1.86458 grams $Na_2B_4O_7$ yielded 1.57250 grams $NaNO_3$
(*f*) 1.97702 grams $Na_2B_4O_7$ yielded 1.03946 grams Na_2CO_3
(*g*) 1.60201 grams $Na_2B_4O_7$ yielded 1.12889 grams Na_2SO_4
(*h*) 2.64768 grams $Na_2B_4O_7$ yielded 1.86597 grams Na_2SO_4

Ans. (*a*) 10.896
(*b*) 10.905
(*c*) 10.901
(*d*) 10.898
(*e*) 10.900
(*f*) 10.903
(*g*) 10.902
(*h*) 10.896

Av.... 10.900

95. In determining the atomic weights of sodium and chlorine, Richards and Wells carried out three series of experiments, the final results of which were as follows:

I. In 10 experiments, 44.5274 grams of NaCl yielded 109.1897 grams of AgCl.

II. In 12 experiments, 49.5007 grams of NaCl were found to be equivalent to 91.3543 grams of Ag.

III. In 10 experiments, 82.6689 grams of Ag yielded 109.8395 grams of AgCl.

Assuming the atomic weight of silver to be 107.920, the atomic weight of chlorine was calculated from the results of Series III, and using the value obtained, the atomic weight of sodium was calculated from the data of Series I and also from the data of Series II. What were the values obtained?

Ans. Cl = 35.470
Na = (*a*) 23.004
(*b*) 23.007

96. In determining the atomic weight of arsenic, Baxter and Coffin converted several samples of Ag_3AsO_4 into AgCl and found the average value for the factor $\frac{3AgCl}{Ag_3AsO_4}$ to be 0.929550. Using the factor $\frac{Ag}{AgCl}$ as found by Richards and Wells to be 0.752632, calculate the percentage of Ag in Ag_3AsO_4. Taking the atomic weight of silver as 107.880 calculate to five figures the atomic weight of arsenic. What would be the percentage error in this last value if the atomic weight of silver were really 107.870?

Ans. 69.9609 per cent; 74.961 per cent; 0.017 per cent.

23. Analysis by Electrolysis.—Quantitative Analysis by means of electrochemical methods is usually restricted to the determination of metals. An electric current is passed, under suitable conditions, through a solution of the salt of a metal, and the metal itself is gradually deposited, usually in the elementary condition, upon one of the electrodes. The calculation of the amount of metal which will be deposited at the end of a given time is founded on Faraday's Laws which may be stated as follows:

1. The mass of any substance deposited at an electrode is proportional to the quantity of electricity which passes through the solution.

2. The amounts of different substances liberated at the electrodes by the passage of the same quantity of electricity are proportional to the equivalent weights of the substances.

Current strength is expressed in terms of the *ampere*, which is defined as that strength of current which, when passed through a solution of silver nitrate under certain standard conditions, will deposit silver at the rate of 0.001118 gram per second.

Quantities of electricity are expressed in terms of the *coulomb*, which is defined as that quantity of electricity which passes through a conductor in 1 second when the current is 1 ampere. That is,

$$Q = It,$$

where Q = quantity of electricity in coulombs
I = current strength in amperes,
t = time in seconds.

From Faraday's first law it follows that the weight of a substance liberated from solution by electrolysis during a given time will be directly proportional to the current strength, and under a given amperage will be directly proportional to the time.

Faraday's second law states that the weights of different substances liberated at the electrodes by a given quantity of electricity are proportional to the respective equivalent weights. The equivalent weight of a substance in this case is the atomic or molecular weight divided by the *change* in valence. It is found by experiment that 96,500 coulombs are required to liberate a gram-equivalent weight (equivalent weight in grams) of any substance. Thus, 96,500 coulombs of electricity are capable of depositing at the cathode:

$\frac{Ag}{1}$ = 107.88 grams of silver from a solution of a silver salt;

$\frac{Fe}{2}$ = 27.92 grams of iron from a solution of a ferrous salt;

$\frac{Fe}{3}$ = 18.61 grams of iron from a solution of a ferric salt.

The value 96,500 coulombs is therefore a unit of quantity in electrochemical measurements and in that capacity it is called a *faraday*. One faraday = 96,500 coulombs = 96,500 ampere-seconds = 26.81 ampere-hours.

The above reactions may be expressed by equations, as follows:

$$(a)\ Ag^{+} + \epsilon \rightarrow Ag$$
$$(b)\ Fe^{++} + 2\epsilon \rightarrow Fe$$
$$(c)\ Fe^{+++} + 3\epsilon \rightarrow Fe$$

where the symbol ϵ represents the electron, or unit of negative electricity. If the equations are considered as representing gram-atomic or gram-molecular ratios, then the symbol represents the faraday. That is, one, two, and three faradays are required to deposit a gram-atomic weight of metal from a solution of silver salt, ferrous salt, and ferric salt respectively.

EXAMPLE I.—How many grams of copper will be deposited in 3 hours by a current of 4 amperes, assuming no other reactions to take place at the cathode?

$$t = 3 \times 3600 = 10{,}800 \text{ seconds}$$

$$\text{Number of coulombs} = It = 4 \times 10{,}800 = 43{,}200.$$

$$\text{1 faraday would deposit } \frac{Cu^{++}}{2} = 31.79 \text{ grams of copper}$$

$$\text{43,200 coulombs would deposit } \frac{43{,}200}{96{,}500} \times 31.79 =$$

14.23 grams Cu. *Ans.*

Faraday's laws apply to each electrode. A current of 1 ampere flowing for 96,500 seconds through a copper sulphate solution is not only capable of depositing $\frac{Cu}{2} = 31.79$ grams of copper at the cathode, but at the same time will liberate $\frac{O}{2} =$ 8.000 grams of oxygen at the anode:

$$Cu^{++} + 2\epsilon \rightarrow Cu \qquad \text{(cathode)}$$
$$H_2O - 2\epsilon \rightarrow 2H^+ + \tfrac{1}{2}O_2 \text{ (anode)}$$

The passage of 2 faradays therefore deposits one gram-atomic weight of copper (=63.57 grams) and liberates ½ mole, or 16 grams of oxygen gas occupying 11.2 liters under standard conditions. As seen from the equation, the acidity of the solution increases by one gram-equivalent ($\simeq$ 1 mole $HNO_3 \simeq$ ½ mole H_2SO_4 etc.) per faraday passed. This gain in acidity may be expressed in terms of acid normality (see Part II, Volumetric Analysis). It is possible to prepare a solution suitable as a standard in acidimetry by electrolyzing a neutral solution of copper sulphate and determining the acid concentration of the resulting solution from the weight of copper deposited.

The electrolysis of a dilute sulphuric acid solution causes the following reactions to take place:

$$2H^+ + 2\epsilon \rightarrow H_2 \qquad \text{(cathode)}$$
$$H_2O - 2\epsilon \rightarrow 2H^+ + \tfrac{1}{2}O_2 \text{ (anode)}$$

The passage of 1 faraday liberates ½ gram-mole of hydrogen (1.008 grams; 11.2 liters under standard conditions) and ¼ gram-mole of oxygen (8.000 grams; 5.6 liters under standard conditions). The total volume of gas evolved per faraday is therefore ¾ mole (16.8 liters). In this electrolysis there is no net change in acidity if the volume of the solution is kept constant, for the loss in acidity at the cathode is balanced by the gain in acidity at the anode.

The electrolysis of a dilute nitric acid solution of lead causes the deposition of lead dioxide on the anode:

$$Pb^{++} + 2H_2O - 2\epsilon \rightarrow PbO_2 + 4H^+ \text{ (anode)}$$
$$2H^+ + 2\epsilon \rightarrow H_2 \qquad \text{(cathode)}$$

One faraday therefore deposits $\frac{PbO_2}{2} = 119.6$ grams of PbO_2,

liberates ½ mole of hydrogen, and increases the acidity by 1 hydrogen equivalent.

EXAMPLE II.—A neutral solution containing 0.4000 gram of copper is electrolyzed until all the copper is plated out, and the electrolysis is continued 7 minutes longer. The volume of the solution is kept at 100 c.c. and the current strength is maintained at an average of 1.2 amperes. Assuming 100 per cent current efficiency, (*a*) how long did it take for the copper to deposit; (*b*) what total volume of gas was evolved during the entire electrolysis; (*c*) what was the acidity of the solution at the end of the electrolysis?

1 faraday deposits $\frac{Cu}{2}$, = 31.79 grams Cu.

Number of faradays to deposit 0.4000 gram Cu = $\frac{0.4000}{31.79}$ = 0.01258.

Time required = $\frac{0.01258 \times 96{,}500}{1.2}$ = 1012 seconds = 16.87 minutes.

Ans.

During deposition of Cu, each faraday (*i.e.*, each ½ mole Cu) corresponds to ¼ mole O_2.

Moles O_2 evolved = 0.01258 × ¼ = 0.003145.

After Cu deposited, number faradays passed = $\frac{7 \times 60 \times 1.2}{96{,}500}$ = 0.005224.

Each faraday evolves ½ mole H_2 and ¼ mole O_2 (see text).

Moles $H_2 + O_2$ evolved = 0.005224 × ¾ = 0.003918.

Total gas evolved = 0.003145 + 0.003918 = 0.007063 moles.

Ans.

During Cu deposition each faraday corresponds to a gain of 1 gram atom of H^+.

After Cu deposition acidity does not change.

Gain in acidity = 0.01258 gram equivalents of H^+. *Ans.*

(Resulting solution is 10 × 0.01258 = 0.1258 normal as an acid.)

In the above calculations involving Faraday's second law, it has been assumed that all the current serves for the decomposition of the substance in question; that is, 100 per cent current

efficiency has been assumed. In actual analyses this is not usually the case. The electrolysis of an acid solution of a copper salt will not only cause the deposition of copper at the cathode, but small amounts of hydrogen will usually be given off at the same electrode before the copper has all plated out. In such cases, the *sum* of the weights of the products discharged at each electrode exactly corresponds to the law. That is, in the copper electrolysis, for each faraday of electricity passed, the number of gram-equivalent weights of copper deposited added to the number of gram-equivalent weights of hydrogen liberated will be unity. In problems of electro analyses, unless otherwise specified, 100 per cent current efficiency may be assumed.

Other electrical units which are frequently used in electro chemical computations are as follows:

The *ohm*, R, is the unit of resistance. It is the resistance offered to a constant current of electricity at 0°C. by a column of mercury 1 square millimeter in cross-section and 106.3 centimeters long.

The *volt*, E, is the unit of electromotive force or electrical pressure. Its relation to the ampere and ohm is expressed by Ohm's Law:

$$E = IR.$$

The *joule*, J, is the unit of work. It is represented by the energy expended in 1 second by a current of 1 ampere against a resistance of 1 ohm:

$$J = EIt = EQ = 10^7 \text{ ergs.}$$

The *watt*, W, is the unit of power. It is represented by the work done at the rate of 1 joule per second

$$W = EI. \quad J = Wt.$$

Problems

97. A 100-watt, 110-volt incandescent lamp is connected in series with an electrolytic cell. What weight of cadmium could be deposited from solution by the current in 30 minutes?

Ans. 0.953 grams.

98. How many minutes will it take for a current of 0.5 ampere to cause the deposition of 500 milligrams of silver from nitric acid solution assuming 80 per cent current efficiency?

Ans. 18.6 minutes.

99. How many coulombs of electricity are required to deposit 0.1000 gram of cobalt from a solution of cobaltous salt? How many amperes would be

required to deposit that amount in 20 minutes, 20 seconds? How many grams of nickel would be deposited under identical conditions?

Ans. 327.3 coulombs.
0.2682 ampere.
0.09951 gram.

100. Under identical conditions of current efficiency, etc., what weight of antimony could be deposited from a thio-antimonate solution in the same length of time required for the deposition of 0.2060 gram of zinc?

Ans. 0.1515 gram.

101. Using a current at 8 volts how much electrical energy is theoretically required to deposit (*a*) 0.100 gram of gold; (*b*) 0.100 gram of mercury from solutions containing these metals in the higher state of oxidation?

Ans. (*a*) 1180 joules.
(*b*) 770 joules.

102. What weight of copper will be deposited from cupric solution by a current of 1.5 amperes during a period of 45 minutes, assuming 100 per cent current efficiency?

Ans. 0.1336 gram.

103. What weights of Cu, of Zn, and of PbO_2 will be deposited in separate electrolytic cells assuming 100 per cent current yield by a current of 0.08 ampere flowing for 30 hours?

Ans. 2.85 grams Cu.
2.93 grams Zn.
10.7 grams PbO_2.

104. Using a rotating electrode, Sand obtained 0.240 gram of copper from a nitric acid solution of copper sulphate in 6 minutes. A current of 10 amperes under 2.8 volts was used. What electrical energy was expended and what was the current efficiency?

Ans. 10,080 joules.
20.2 per cent.

105. How many grams of tin will be deposited from a solution of stannous salt by a current of 5.5 amperes in 25 minutes assuming 3.94 per cent current efficiency?

Ans. 0.200 gram.

106. In a series of experiments, Amberg showed the effect on the rate of deposition of palladium brought about by stirring the solution of electrolyte. With a stirrer revolving 620 times per minute, 0.60 gram of Pd was deposited in 4 hours, 27 minutes; at 800 revolutions per minute, 0.95 gram was deposited in 4 hours, 30 minutes; at 1000 revolutions per minute, 2.3 grams were deposited in 6 hours. An average current strength of 0.25 ampere was used throughout. Calculate the current efficiency in each case.

Ans. 27.1 per cent.
42.4 per cent.
77.0 per cent.

107. Using a rotating electrode, Langness found that with a current of 17 amperes and a potential of 10 volts, 0.200 gram of platinum could be deposited in 5 minutes from a solution of potassium chloroplatinate. How much electrical energy was expended per second? What quantity of electricity was used? What was the current efficiency?

Ans. 170 joules.
5,100 coulombs.
7.75 per cent.

108. What quantity of electricity is required for (*a*) the electrolytic deposition of 1.196 grams of PbO_2; (*b*) the liberation of 0.800 gram of oxygen gas; (*c*) the liberation of 30.0 c.c. of chlorine when measured under standard conditions (one molecular weight in grams occupies 22.4 liters)?

Ans. (*a*) 965 coulombs.
(*b*) 9,650 coulombs.
(*c*) 259 coulombs.

109. For how long a time must a current of 1 ampere be passed through a dilute solution of sulphuric acid in order to liberate a total volume of 600 c.c. of gas when measured dry and under standard conditions (one molecular weight in grams occupies 22.4 liters)?

Ans. 57.4 minutes.

110. With a current of 1 ampere, what weight of silver would be deposited in 1 minute in a silver coulometer? What volume of gas (under standard conditions) would be evolved in 1 minute in a water coulometer? (Gram-molecular volume = 22.4 liters).

Ans. 0.06708 gram.
10.44 c.c.

111. Pure crystals of copper sulphate are dissolved in water and the solution is electrolyzed until the solution is colorless. The cathode gains 0.4280 gram. What is the acidity of the solution in terms of moles of H_2SO_4?

Ans. 0.006731 moles.

112. A current of 0.5 ampere is passed through a dilute acid solution of an alloy containing 0.5000 gram of copper, 0.2000 gram of zinc, and 0.1000 gram of lead. Assuming 100 per cent efficiency compute the total gain in acidity in terms of moles of H_2SO_4 (*a*) at the end of the PbO_2 deposition at the anode, (*b*) at the end of the Cu deposition at the cathode, (*c*) after the current has been continued 5 minutes longer. What volume of gas (standard conditions) has been evolved during the entire process?

Ans. (*a*) 0.0009652 moles.
(*b*) 0.008347 moles.
(*c*) 0.008347 moles.
108.8 c.c.

113. Carbonic acid in solution may be reduced to formic acid by means of the electric current, the reaction corresponding to the equation:

$$H_2CO_3 + 2H^+ + 2\epsilon \rightarrow HCOOH + H_2O.$$

The following data are given by Allmand as a practical illustration of the work of Coehn and Jahn (*Berichte*, **37**, 2836):

Carbon dioxide gas is continually bubbled through a saturated solution of K_2SO_4 which serves as an electrolyte. A water coulometer and a copper coulometer are connected in series with the cell and a current is passed for 8 hours. Occasionally, the mixture of hydrogen and carbon dioxide which continually pass away from the cathode is collected, and after absorbing the CO_2 by caustic potash, the volume of the residual hydrogen is compared with the volume of the electrolytic gas evolved in the water coulometer during the same period. On one such occasion, the volume of the residual hydrogen is 10.6 c.c. and the volume of gas from the water coulometer is 60.0 c.c. At the end of the 8 hours, 1.23 grams of formic acid (HCOOH) have been formed and 2.335 grams of copper have been deposited in the copper coulometer.

Calculate (*a*) the current efficiency during the period when the above gas sample was taken; (*b*) the current efficiency and average amperage during the entire electrolysis.

Ans. (*a*) 73.5 per cent.
(*b*) 72.8 per cent.
0.246 ampere.

CHAPTER VI

CALCULATIONS FROM REPORTED PERCENTAGES

24. Calculations Involving the Elimination or Introduction of a Constituent.—It is occasionally necessary to eliminate from or introduce into a report of an analysis one or more constituents and calculate the results to a new basis. Thus, a mineral may contain hygroscopic water which is not an integral part of the molecular structure. After complete analysis, it may be desirable to calculate the results to a dry basis as being more representative of the mineral under normal conditions. On the other hand, a material may contain a very large amount of water, and because of the difficulty of proper sampling, a small sample may be taken for the determination of the water while the bulk of the material is dried, sampled, and analyzed. It may then be desirable to convert the results thus obtained to the basis of the original wet sample. This applies equally well to constituents other than water, and in any case, the method by which these calculations are made is based upon the fact that the constituents other than the ones eliminated or introduced are all changed in the same proportion, and the total percentage must remain the same.

EXAMPLE I.—A sample of lime gave the following analysis:

CaO	90.15 per cent
MgO	6.14 per cent
$Fe_2O_3 + Al_2O_3$	1.03 per cent
SiO_2	0.55 per cent
$H_2O + CO_2$ (by loss on ignition)	2.16 per cent
	100.03 per cent.

What is the percentage composition of the ignited sample assuming the volatile constituents to be completely expelled?

In the sample as given, the total percentage of all constituents is 100.03. The slight variation from the theoretical 100 per cent

is due to experimental errors in the analysis. The total per centage of non-volatile constituents is 100.03 − 2.16 = 97.87 per cent. Ignition of the sample would therefore increase the percentage of each of the non-volatile constituents in the ratio of 100.03 to 97.87, and the percentage composition of the ignited sample would be:

$$\left.\begin{aligned}
\text{CaO} &= 90.15 \times \frac{100.03}{97.87} = 92.14 \text{ per cent} \\
\text{MgO} &= 6.14 \times \frac{100.03}{97.87} = 6.28 \text{ per cent} \\
\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 &= 1.03 \times \frac{100.03}{97.87} = 1.05 \text{ per cent} \\
\text{SiO}_2 &= 0.55 \times \frac{100.03}{97.87} = 0.56 \text{ per cent}
\end{aligned}\right\} \textit{Ans.}$$

100.03 per cent

Example II.—If the original sample of lime mentioned in the preceding problem were heated only sufficiently to reduce the percentage of volatile constituents from 2.16 per cent to 0.50 per cent, what would be the percentage composition of the product?

In the original sample, the total percentage of non-volatile constituents is 100.03 − 2.16 = 97.87 per cent. In the ignited sample the total percentage of residual constituents would be 100.03 − 0.50 = 99.53 per cent. The loss of volatile matter would therefore have caused the percentage of the various constituents to increase in the ratio of 99.53 to 97.87. Hence the percentage composition would be:

$$\left.\begin{aligned}
\text{CaO} &= 90.15 \times \frac{99.53}{97.87} = 91.68 \text{ per cent} \\
\text{MgO} &= 6.14 \times \frac{99.53}{97.87} = 6.24 \text{ per cent} \\
\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 &= 1.03 \times \frac{99.53}{97.87} = 1.05 \text{ per cent} \\
\text{SiO}_2 &= 0.55 \times \frac{99.53}{97.87} = 0.56 \text{ per cent} \\
\text{Volatile matter} &= 0.50 \text{ per cent}
\end{aligned}\right\} \textit{Ans.}$$

100.03 per cent

Problems

114. The percentage of copper in a sample of copper ore with a moisture content of 8.27 per cent is found to be 36.47 per cent. Calculate the percentage on a dry sample.

Ans. 39.76 per cent.

115. A sample of coal as taken from the mine contains 8.32 per cent ash. An air-dried sample of the same coal contains 10.03 per cent ash and 0.53 per cent moisture. Calculate the percentage of moisture in the original sample.

Ans. 17.50 per cent.

116. Lime is to be manufactured by the ignition of a sample of dolomite. The only data as to the composition of the dolomite are as follows:

96.46 per cent $CaCO_3 + MgCO_3$
2.21 per cent SiO_2
10.23 per cent MgO
1.33 per cent H_2O.

The analysis of the lime shows no water and 1.37 per cent carbon dioxide. Calculate the percentage of CaO, MgO, and SiO_2 in the lime.

Ans. CaO = 76.14 per cent.
MgO = 18.52 per cent.
SiO_2 = 4.00 per cent.
CO_2 = 1.37 per cent.

117. The oil in a sample of paint is extracted and the residual pigment is found to be 66.66 per cent of the original weight. An analysis of the pigment gives:

Zinc oxide = 24.9 per cent
Lithopone = 51.6 per cent
Barytes = 23.5 per cent
100.0 per cent

Calculate the percentage composition of the original paint.

Ans. Zinc oxide = 16.6 per cent.
Lithopone = 34.4 per cent.
Barytes = 15.7 per cent.
Vehicle = 33.3 per cent.

118. The same sample of iron ore is analyzed by two chemists. Among other constituents, Chemist A reports:

Moisture = 1.62 per cent
Iron = 43.92 per cent

Chemist B reports:

Moisture = 0.96 per cent
Iron = 44.36 per cent

Calculate the percentage of iron in both cases on a dry sample. Analysis of a dry sample shows A to be correct. What is the error and percentage error in the constituent iron in B's analysis as reported?

Ans. A = 44.64 per cent.
B = 44.79 per cent.
0.15 per cent; 0.34 per cent.

119. A cargo of wet coal is properly sampled and the loss in weight at 105°C. is determined as 10.6 per cent. The dried sample is used for the analysis of other constituents, as follows:

Volatile combustible matter = 21.60 per cent
Coke = 60.04 per cent
Ash = 18.36 per cent

The air-dried coal (moisture content = 1.35 per cent) costs $4.40 a ton at the mine. What is its percentage of ash? Neglecting other factors except water content, calculate the value of the coal as received.

Ans. 18.11 per cent.
$3.99 a ton.

120. A sample of coal gives the following analysis:

Moisture = 3.76 per cent
Volatile combustible matter = 20.38 per cent
Coke = 64.01 per cent
Ash = 11.85 per cent

100.00 per cent

The coal is to be sold on the following specifications:

Moisture = not over 5 per cent
Volatile combustible matter = to exceed 20 per cent
Ash = not over 12 per cent

(*a*) Will a dry sample cover specifications?
(*b*) Will a sample containing the limit of moisture cover specifications?
(*c*) What is the analysis of the coal as delivered if specifications are covered and the amount of ash is as high as possible?

Ans. (*a*) No.
(*b*) Yes.
(*c*) Moisture = 2.52 per cent.
Volatile combustible matter = 20.64 per cent.
Coke = 64.84 per cent.
Ash = 12.00 per cent.

100.00 per cent.

121. The moisture content of a sample of $Al_2(SO_4)_3.18H_2O$ is reduced from the theoretical to 7.36 per cent. Calculate the analysis of the partly dried

material reporting percentage of Al_2O_3, SO_3, and H_2O. The original salt costs \$0.0262 per pound. Calculate the cost of the dried material, considering only the loss in water content.

Ans. Al_2O_3 = 27.64 per cent.
SO_3 = 64.98 per cent.
H_2O = 7.36 per cent.
\$0.0473.

122. "Air-dry" paper pulp is considered as containing 10 per cent of water. A sample of wet pulp weighs 737.1 grams and when heated to "bone-dryness" weighs 373.6 grams. What is the percentage of "air-dry" pulp in the original sample?

Ans. 56.30 per cent.

123. A sample of lime gives the following analysis:

CaO	= 75.12 per cent
MgO	= 15.81 per cent
SiO_2	= 2.13 per cent
Fe_2O_3	= 1.60 per cent
CO_2	= 2.16 per cent
H_2O	= 3.14 per cent
	99.96 per cent

What is the percentage of each constituent after superficial heating in which the CO_2 content has been reduced to 1.08 per cent and the water content to 1.00 per cent?

Ans. CaO = 77.66 per cent.
MgO = 16.35 per cent.
SiO_2 = 2.21 per cent.
Fe_2O_3 = 1.66 per cent.
CO_2 = 1.08 per cent.
H_2O = 1.00 per cent.

99.96 per cent.

25. Calculation of Molecular Formulae from Chemical Analyses.—Given a compound of unknown composition, a chemical analysis will determine the proportion in which the constituents of the compound exist. The results of such an analysis may then be used to calculate the empirical formula of the compound. Thus, the analysis of a certain salt gives the following results:

Zinc	47.96 per cent
Chlorine	52.04 per cent
	100.00 per cent

Dividing the percentage of each constituent by its atomic weight will give the number of gram-atomic weights of that constituent in 100 grams of the compound. In 100 grams of the above salt there are present $\frac{47.96}{65.38} = 0.7335$ gram-atomic weight of zinc, and $\frac{52.04}{35.46} = 1.4674$ gram-atomic weights of chlorine. These numbers are seen to be in the ratio of 1 to 2. The empirical formula of the salt is therefore $ZnCl_2$, although as far as the above analysis is concerned, the actual formula might be Zn_2Cl_4, Zn_3Cl_6, or any other whole multiple of the empirical formula. In general, the determination of the molecular weight of a compound is necessary in order to determine which multiple of the empirical formula will give the actual formula. The usual methods of establishing molecular weights by means of vapor density, freezing-point lowering, boiling-point raising, and other physicochemical phenomena should already be familiar to the student (see also Sec. 22).

The calculation of molecular formulae plays an important part in the analysis of natural minerals. A careful analysis furnishes a means of establishing the empirical formula of a mineral of high degree of purity, although its actual formula is usually impossible to determine. The method of calculation is similar to that of the preceding example, except that the basic constituents of a mineral are usually expressed in terms of their oxides. If the percentage of each constituent is divided by its molecular weight, the number of moles (gram-molecular weights) of that constituent in 100 grams of the mineral is obtained. From the ratios of the number of moles of the various constituents thus obtained, the formula of the mineral may be determined. It should be remembered, however, that the analytical methods used in the determination of some constituents may give results which are of relatively low degree of accuracy. It can hardly be expected, therefore, that the number of moles of the various constituents will stand to one another *exactly* in the ratio of small whole numbers, although in the actual molecule (except in cases involving isomorphism discussed below) they must do so. Indeed in many cases, some judgment must be exercised in order to determine from the analysis the true molal ratios of the constituents in the molecule.

A slide rule will be found to be almost indispensable for this purpose, since, with one or two settings of the rule, all possible ratios are visible.

EXAMPLE I.—The analysis of a certain mineral gives the following results:

Al_2O_3	38.07 per cent
K_2O	17.70 per cent
CaO	10.46 per cent
SiO_2	33.70 per cent
	99.93 per cent

What is the empirical formula of the mineral?

In 100 grams of the mineral there are present:

$$\frac{38.07}{Al_2O_3} = \frac{38.07}{102.0} = 0.3733 \text{ mole of } Al_2O_3$$

$$\frac{17.70}{K_2O} = \frac{17.70}{94.20} = 0.1879 \text{ mole of } K_2O$$

$$\frac{10.46}{CaO} = \frac{10.46}{56.07} = 0.1865 \text{ mole of CaO}$$

$$\frac{33.70}{SiO_2} = \frac{33.70}{60.3} = 0.559 \text{ mole of } SiO_2$$

It is seen that the number of moles of these constituents are nearly enough in the ratio of 2:1:1:3 to be within the limits of experimental error. The molecule is therefore made up of $2Al_2O_3.K_2O.CaO.3SiO_2$, and may be written: $Al_4K_2CaSi_3O_{14}$.

26. Calculation of Formulae of Minerals Exhibiting Isomorphic Replacement.—Complications arise in the calculation of formulae in the cases of minerals exhibiting isomorphic replacement—that is, the partial replacement of one constituent by one or more other constituents having the same general properties. It therefore happens that, due to different degrees of replacement, samples of the same kind of mineral obtained from different localities often give on analysis results which apparently bear little resemblance to one another.

As a general rule, a constituent may be replaced only by another of the same type and valence. Thus, Fe_2O_3 is often partially or wholly replaced by Al_2O_3 and *vice versa*. CaO may be replaced by MgO, MnO, FeO, etc. Exceptions are sometimes

met with, but for purposes of calculation, this assumption may be safely made. Since the isomorphic replacement occurs in no definite proportion, it follows that the molal amounts of the constituents in such minerals do not necessarily bear any simple relation to one another. On the other hand, if constituent *B* partially replaces constituent *A*, since the valences are the same, the *sum* of the molal amounts of *A* and *B* would be the same as the molal amount of *A* if it had not been replaced. Consequently, when the molal quantities of the constituents of a mineral in themselves bear no simple ratio to one another, the quantities of constituents of the same type should be combined in an effort to obtain *sums* which do exist in ratios of simple whole numbers.

EXAMPLE I.—A certain mineral gives the following analysis:

Al_2O_3	20.65 per cent
Fe_2O_3	7.03 per cent
CaO	27.65 per cent
SiO_2	44.55 per cent
	99.88 per cent

What is the empirical formula?

The number of moles of each constituent in 100 grams of the mineral is found to be:

$$\left.\begin{aligned} \frac{20.65}{Al_2O_3} &= 0.2025 \text{ mole of } Al_2O_3 \\ \frac{7.03}{Fe_2O_3} &= 0.0440 \text{ mole of } Fe_2O_3 \end{aligned}\right\} = 0.2465 \text{ mole}$$

$$\frac{27.65}{CaO} = 0.4932 \text{ mole of CaO}$$

$$\frac{44.55}{SiO_2} = 0.7389 \text{ mole of } SiO_2$$

Only when the molal quantities of the first two constituents are combined are all the above numerical results found to be in simple ratio to one another, these being approximately as 1:2:3. This shows isomorphic replacement between Fe_2O_3 and Al_2O_3, and the formula of the mineral may therefore be written:

$$(Al,Fe)_2O_3.2CaO.3SiO_2$$

or

$$Ca_2(Al,Fe)_2Si_3O_{11}.$$

Problems

124. From the following percentage composition of ethyl-amine calculate its empirical formula:

Carbon	=	53.27 per cent
Hydrogen	=	15.65 per cent
Nitrogen	=	31.08 per cent
		100.00 per cent

Ans. C_2H_7N.

125. Calculate the empirical formula of the compound having the following composition:

Calcium	=	23.53 per cent
Hydrogen	=	2.37 per cent
Phosphorus	=	36.49 per cent
Oxygen	=	37.61 per cent
		100.00 per cent

Ans. $Ca(H_2PO_2)_2$.

126. Calculate the empirical formula of an organic compound having the following composition:

Carbon	=	68.83 per cent
Hydrogen	=	4.96 per cent
Oxygen	=	26.21 per cent
		100.00 per cent

Ans. $C_7H_6O_2$.

127. Show that the following analysis of di-ethyl-hydrazine agrees with the formula $(C_2H_5)_2{:}N.NH_2$:

Carbon	=	54.55 per cent
Hydrogen	=	13.74 per cent
Nitrogen	=	31.80 per cent
		100.09 per cent

128. Calculate the formula of a compound which has a molecular weight of 90.03 and is composed of

Carbon	=	26.67 per cent
Hydrogen	=	2.24 per cent
Oxygen	=	71.09 per cent
		100.00 per cent

Ans. $H_2C_2O_4$.

129. An analysis of prehnite gave the following results:

H_2O =	4.35 per cent
CaO =	27.15 per cent
Al_2O_3 =	24.85 per cent
SiO_2 =	43.74 per cent
	100.09 per cent

Calculate the empirical formula of the mineral.

Ans. $H_2Ca_2Al_2Si_3O_{12}$.

130. Dana gives the composition of vivianite as follows:

P_2O_5 =	28.3 per cent
FeO =	43.0 per cent
H_2O =	28.7 per cent
	100.0 per cent

Show that this conforms to the formula $Fe_3P_2O_8.8H_2O$.

131. A certain compound contains only the following constituents: CaO, Na_2O, SO_3. The percentages of these constituents are in the respective approximate ratios of 9:10:26. What is the empirical formula of the compound?

Ans. $Na_2CaS_2O_8$.

132. The percentage composition of a certain silicate is given below. Calculate the empirical formula of the mineral.

K_2O =	21.53 per cent
Al_2O_3 =	23.35 per cent
SiO_2 =	55.12 per cent
	100.00 per cent

Ans. $KAlSi_2O_6$.

133. A certain compound of carbon and oxygen has an approximate molecular weight of 290, and by analysis is found to contain 50 per cent by weight of each constituent. What is the formula of the compound?

Ans. $C_{12}O_9$.

134. What is the empirical formula of a simple basic cupric carbonate which, according to Rogers, contains 57.4 per cent Cu and 8.1 per cent H_2O?

Ans. $Cu_2(OH)_2CO_3$.

135. The composition of bismutite is given by Ramm as

CO_2 =	6.38 per cent
Bi_2O_3 =	89.75 per cent
H_2O =	3.87 per cent
	100.00 per cent

Calculate the empirical formula.

Ans. $2Bi_2C_3O_{18}.9H_2O$.

136. What is the empirical formula of a silicate of the following composition?

CaO =	24.72 per cent
MgO =	11.93 per cent
FeO =	10.39 per cent
SiO_2 =	53.09 per cent
	100.13 per cent

Ans. $Ca(Mg, Fe)(SiO_3)_2$.

137. A silicate gives the following analysis. If two-thirds of the water exists as water of crystallization what is the empirical formula?

H_2O =	17.22 per cent
CaO =	8.22 per cent
Na_2O =	0.76 per cent
Al_2O_3 =	16.25 per cent
SiO_2 =	57.48 per cent
	99.93 per cent

Ans. $H_4(Ca, Na_2)Al_2(SiO_3)_6.4H_2O$.

138. Calculate the empirical formula of a mineral which analyzes as follows:

MnO =	46.36 per cent
CaO =	6.91 per cent
SiO_2 =	46.83 per cent
	100.10 per cent

Ans. $(Mn, Ca)SiO_3$.

139. The analysis of samples of microcline and of albite are given below. Show that these minerals are of the same type and give the general empirical formula. Assume the percentages of silica and alumina to be the most reliable.

Microcline:	Na_2O =	1.61 per cent
	K_2O =	13.56 per cent
	Al_2O_3 =	19.60 per cent
	SiO_2 =	64.79 per cent
		99.56 per cent
Albite:	Na_2O =	11.11 per cent
	K_2O =	0.51 per cent
	CaO =	0.38 per cent
	Al_2O_3 =	19.29 per cent
	SiO_2 =	68.81 per cent
		100.10 per cent

140. Calculate the empirical formula of axinite from the following analysis:

H_2O =	1.58 per cent
CaO =	19.63 per cent
FeO =	9.54 per cent
MnO =	3.01 per cent
Al_2O_3 =	17.92 per cent
B_2O_3 =	6.12 per cent
SiO_2 =	42.23 per cent
	100.03 per cent

Ans. $HCa_2(Fe, Mn)Al_2B(SiO_4)_4$.

141. A sample of the mineral biotite gave the following analysis:

H_2O =	1.10 per cent
FeO =	9.60 per cent
Al_2O_3 =	22.35 per cent
K_2O =	14.84 per cent
MgO =	12.42 per cent
SiO_2 =	39.66 per cent
	99.97 per cent

What is the empirical formula of the mineral?

Ans. $(H, K)_2 (Mg, Fe)_2 Al_2Si_3O_{12}$.

PART II
VOLUMETRIC ANALYSIS

CHAPTER VII

CALIBRATION OF MEASURING INSTRUMENTS

27. Measuring Instruments in Volumetric Analysis.—The principle of Volumetric Analysis differs from that of Gravimetric Analysis in that instead of isolating and weighing a product of a reaction directly or indirectly involving the desired substance, the volume of a reagent required to bring about a direct or indirect reaction with that substance is measured. From the volume of the reagent and its concentration, the weight of the substance is calculated.

Since Volumetric Analysis makes use of exact volume relationships, it is essential first to adopt a definite standard for a unit volume, and then to calibrate all measuring instruments to conform to this standard. The measuring instruments most often used are burettes, pipettes, and measuring flasks, and the experimental methods of calibrating them may be found in any standard text-book on Quantitative Analysis. (Ref. Treadwell-Hall: "Analytical Chemistry," 6th ed., vol. 2, pp. 441–456.)

28. Calculation of the True Liter.—A *liter* is the volume occupied by 1 kilogram of water at the temperature of its maximum density (approximately 4°C.). A *cubic centimeter* is the volume occupied by a cube 1 centimeter on a side and is almost exactly one one-thousandth of a liter. In calibrating a vessel, since the cubical content of the vessel holding the water to be weighed varies with the temperature, it is evident that the temperature of the container must be included in the specifications. Instead of taking the corresponding temperature of 4°C., the temperature of 20°C. has been accepted as the *normal temperature* by the Bureau of Standards at Washington. Other temperatures are sometimes used, particularly on older forms of

apparatus, and it is therefore important in using measuring apparatus to know which temperature has been taken as the standard. In this book, unless otherwise specified, the value 20°C. will be taken as the normal temperature.

To contain a *true liter* then, a flask must be so marked that at 20°C. its capacity will be equal to the volume of water which at 4°C. weighs 1 kilogram in vacuo. From the density of water at different temperatures (Table V, Appendix), the coefficient of cubical expansion of glass (0.000026), and the relationship existing between the weight of a substance in air and the weight in vacuo (Sec. 9), it is possible to calculate the amount of water to be weighed into a container in order that it shall occupy a true liter at any given temperature.

Example I.—How much water at 25°C. should be weighed in air with brass weights so that when placed in a flask at the same temperature and under normal barometric pressure it will occupy 1 true liter at 20°C.?

Density of water at 25°C. = 0.99707 (Table V).

At 4°C. and in vacuo, 1000 grams of water, by itself, will occupy 1 true liter.

At 25°C. and in vacuo, 1000×0.99707 gram of water will occupy 1 true liter.

At 25°C. and in air, the weight of water is found by substituting in the formula:

$$W^0 = W + \left(\frac{W}{s} - \frac{W}{s'}\right)a$$

and solving for W (see Sec. 9).

Thus,

$$997.07 = W + \left(\frac{W}{0.99707} - \frac{W}{8.0}\right)0.0012$$

Since the term to the right of the plus sign is required to only two significant figures, it is sufficiently accurate to write

$$997.07 = W + \left(\frac{1000}{1.0} - \frac{1000}{8.0}\right)0.0012$$

whence,

$$W = 996.02 \text{ grams.}$$

Theoretically, to contain a true liter, the flask must be at 20°C. and yet contain this weight of water at 25°C. Actually, the

temperature of the flask is also 25°C. It has therefore expanded, the cubical content is greater, and the true liter volume is also greater. The coefficient of cubical expansion of glass is 0.000026, and the increase in volume from 20 to 25°C. is $1000 \times 0.000026(25 - 20) = 0.13$ c.c. This volume is represented by $0.13 \times 0.99707 = 0.13$ gram of water. The required weight of water is therefore:

$$996.02 + 0.13 = 996.15 \text{ grams.} \qquad \textit{Ans.}$$

A general formula may now be written for calculating the weight of water required for a true liter:

$$W = \frac{1000 \times d}{1 + \frac{a}{d} - \frac{a}{s'}} + [1000 \times d \times c(t - 20)],$$

in which W = grams of water required for 1 true liter,
t = temperature of water and flask,
d = density of water at $t°$,
a = weight of 1 c.c. of air under given conditions,
s' = specific gravity of balance weights,
c = coefficient of cubical expansion of the container

(The values of these last three terms are usually 0.0012, 8.0, and 0.000026 respectively.)

29. Calculation of the Mohr Liter.—To avoid the tedious computation involved in the use of the true liter, a simpler standard has been proposed for ordinary analytical work, although it is not often used now. This makes use of the so-called Mohr liter. The Mohr liter is the volume of a kilogram of water at 15°C., as weighed in air with brass weights, and under standard barometric conditions. Other temperatures are sometimes used for this standard, notably 15.5, 17.5, and 20°C.

If a flask is to be calibrated to contain a Mohr liter, and water at a temperature different from the standard chosen is used, the method of calculation is similar to, although simpler than, that explained in the preceding section.

EXAMPLE I.—How much water at 25°C. must be weighed into a flask in order to occupy a Mohr liter at 15°C.?

Density of water at 15°C. = 0.99913 (Table V).

Density of water at 25°C. = 0.99707.

Grams of water at 25°C. to occupy the same volume as 1 kilogram of water at 15°C. $= 1000 \times \frac{0.99707}{0.99913} = 997.96$.

Increase in cubical content of flask from 15 to 25°C. $= 1000 \times 0.000026(25 - 15)$ (see preceding section) $= 0.26$ c.c., corresponding to $0.26 \times 0.99707 = 0.26$ gram of water.

Total weight of water required $= 997.96 + 0.26 = 998.22$ grams. *Ans.*

These two examples show that the correction for the expansion or contraction of the container is in each case small compared to the quantity to which it is added. Consequently, only an approximate value containing two or three significant figures need be used. Indeed, in the case of instruments of 50-c.c. content or less, and for small differences in temperature, this correction may ordinarily be neglected.

Problems

142. Calculate accurately the amount of water which should be weighed into a tared flask at 18°C. and 770-mm. pressure against brass weights in order that the flask may be marked to contain exactly 250 true cubic centimeters.

Ans. 249.37 grams.

143. Calculate accurately the number of grams of water which should be weighed into a flask at 20°C. against brass weights in order that the flask shall contain a Mohr liter (15°C.).

Ans. 999.23 grams.

144. What is the difference between the number of grams of water to be weighed at 17°C. into a 500-c.c. flask against brass weights to calibrate the flask according to the Mohr standard at 20°C. and the number of grams of water to be weighed at the same temperature and normal barometric pressure to mark the flask to contain 500 true cubic centimeters?

Ans. 1.42 grams.

145. A flask which has been marked to contain 1 true liter is filled with water at 15°C. to the mark and the temperature of the water is allowed to rise to 25°C. How many millimeters above the mark does the water now stand (inner diameter of the neck of the flask = 15.0 millimeters)?

Ans. 10.2 millimeters.

146. In calibrating a flask to contain ½ true liter, if the water is weighed at 26°C. against brass weights, what percentage error would be introduced in the weight of water necessary if the expansion of glass were neglected? What weight of water should be taken?

Ans. 0.016 per cent.
498.07 grams.

147. What is the true volume of a flask that contains 746.24 grams of water at 30°C. when weighed in air against brass weights?

Ans. 750.06 c.c.

148. A flask is accurately marked to contain 1 true liter and the inner diameter of the neck of the flask is 16.0 millimeters. If 996.00 grams of water are weighed out in air against brass weights at 20°C. and placed in the flask at this temperature, how far above or below the true liter mark does the meniscus of the water lie?

Ans. 5.9 millimeters below.

CHAPTER VIII

CONCENTRATION OF SOLUTIONS

30. Standard Solutions.—Volumetric Analysis requires the use of solutions containing a known weight of solute in a definite volume of solution; that is, it involves solutions of known concentration. Such are called *standard* solutions, and the term is applied only to cases where the concentration is known to a precision in keeping with the other numerical data involved.

31. Unit Weight per Unit Volume.—Of the various methods of expressing concentration, possibly the simplest to understand, although the most cumbersome to use, is based upon the number of unit weights of substance contained in a unit volume of solution; for example, the number of grams of solute contained in a liter of solution. This method complicates even the simplest volumetric calculations, since solutions of the same concentration bear no simple relation to each other as far as volumes involved in chemical reactions are concerned. Chemical substances which enter into reaction do so upon a molecule to molecule basis and not upon a gram to gram basis. Thus, suppose a solution of hydrochloric acid contains 5 grams of HCl per liter, and a solution of sodium hydroxide contains 5 grams of NaOH per liter. To calculate the volume of the acid required to neutralize a given volume of the base would involve the use of the ratio of the molecular weights of the two compounds in the way explained and illustrated in Sec. 16. In volumetric determinations involving more complicated reactions and especially requiring the use of several standard solutions, the computations by this method would be tedious.

32. Percentage Composition.—The concentration of a solution is sometimes expressed according to its percentage (by weight) composition. A 1 per cent solution of sodium chloride, for example, contains 1 gram of the salt in 100 grams of solution, or 10 grams of the salt per kilogram of solution. In some branches of chemistry a 1 per cent solution is considered to be 1 gram of

solute per 100 c.c. of solvent, and sometimes it is considered to be 1 gram of solute in 100 grams of solvent. This method of expressing concentration is therefore confusing as well as cumbersome, and offers no advantages.

33. Molal Concentration.—A *mole* or *gram-molecular weight* of an element or compound is the molecular weight of the substance expressed in grams. Thus, 58.46 grams of sodium chloride (NaCl), 40.01 grams of sodium hydroxide (NaOH), and 126.06 grams of oxalic acid ($H_2C_2O_4.2H_2O$) constitute a mole in each case.

A molal solution is one containing a mole of substance dissolved in a liter of *solution*. A gram-molecular weight of substance dissolved in a liter of *water* does not constitute a molal solution, for the resulting solution never occupies exactly a liter. In certain computations involving ionic dissociation, a molal solution is occasionally taken as a mole of solute in 1000 c.c. of water, but this standard is never used in general analytical work. A liter of molal sulphuric acid solution contains 98.08 grams of H_2SO_4; a liter of half-molal sulphuric acid solution contains 49.04 grams of H_2SO_4. It must be emphasized in this particular case that 98.08 grams of H_2SO_4 does not mean 98.08 grams of the ordinary *concentrated* sulphuric acid, but of hydrogen sulphate. The concentrated acid contains about 96 per cent of the latter.

Since 1 mole of hydrochloric acid reacts with 1 mole of sodium hydroxide, a certain volume of sodium hydroxide solution will be exactly neutralized by an equal volume of hydrochloric acid of the same molal concentration, or twice the volume of hydrochloric acid of one-half the molal concentration of the sodium hydroxide. One molecule of hydrogen sulphate will neutralize 2 molecules of sodium hydroxide:

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + H_2O.$$

To neutralize a certain volume of sodium hydroxide solution, only one-half that volume of sulphuric acid of the *same* molal concentration would be required. Volumetric calculations are therefore greatly simplified when concentrations are expressed in terms of moles of substance per unit volume of solution, for when so expressed, the volumes of reacting solutions of the same molal concentration, although not necessarily equal, bear simple relations to each other.

EXAMPLE I.—What volume of 0.6380 molal potassium hydroxide solution will neutralize 430.0 c.c. of 0.4000 molal sulphuric acid?

1 mole $H_2SO_4 \simeq 2$ moles KOH

430.0 c.c. of 0.4000 molal solution contains

$$\frac{430.0}{1{,}000} \times 0.4000 = 0.1720 \text{ mole } H_2SO_4$$

0.1720 mole $H_2SO_4 \simeq 0.3440$ mole KOH

1 c.c. KOH contains 0.0006380 mole KOH

$$\text{Volume required} = \frac{0.3440}{0.0006380} = 539.3 \text{ c.c. } \textit{Ans.}$$

34. Normal Concentration.—The method of expressing concentration which is most convenient, and in the end simplest to use in volumetric calculations, is based upon the number of *equivalents* of solute in a unit volume of solution.

The *equivalent weight* of an element or compound is that weight of it which will involve in reaction one atomic weight of hydrogen, or that weight of any other element or radical which in turn will involve in reaction one atomic weight of hydrogen. This definition holds in all cases but is applied differently to acidimetric reactions than to oxidation and reduction processes or to precipitation methods. The application of equivalent weights to these types of chemical reaction will be taken up individually under their respective headings. It may be said in passing that (1) in acidimetry and alkalimetry the equivalent weight of a substance is the atomic or molecular weight of that substance divided by the number of hydrogen atoms directly involved in the neutralization process of that atom or molecule; (2) the equivalent weight of a substance which is oxidized or reduced is expressed by dividing the atomic or molecular weight of the substance by the change in valence which that atom or molecule undergoes in the reaction in question; (3) the equivalent weight of a substance involved in a precipitation process is found by dividing its atomic or molecular weight by the actual valence of the reacting constituent.

The *milliequivalent weight* is one one-thousandth the value of the equivalent weight.

The *gram-equivalent weight* is the equivalent weight expressed in grams.

A *normal solution* of an element or compound is one containing one gram-equivalent weight of the substance in 1 liter of *solution* (not of solvent). A normal solution therefore contains one gram-milliequivalent weight per cubic centimeter of solution.

A two-normal solution is one containing in a unit volume twice the weight of solute contained in its normal solution. For the sake of brevity in writing, such concentration is often written 2 N.

A half-normal solution is one containing in a unit volume one-half the weight of solute contained in its normal solution, and this concentration may be expressed as 0.5 N, ½ N or N/2. The concentration of a normal solution is expressed simply as N.

Since the concentrations of solutions used in volumetric analyses are usually found experimentally, the concentrations cannot always be expressed by whole numbers. They are more likely to be expressed as decimal fractions, for example, 0.1372 N or 0.05063 N. The *normal value* of a solution is therefore the relation of its concentration to the normal concentration. The word "*normality*" is often used to mean the same as normal value and is so used in this book.

35. Divisions of Volumetric Analysis.—It is customary to divide the reactions of Volumetric Analysis into three groups, namely,

(*a*) Acidimetry and Alkalimetry,

(*b*) Oxidation and Reduction Methods,

(*c*) Saturation or Precipitation Methods,

and so far as calculations involving concentrations of standard solutions are concerned, it will be less confusing to take up each group separately, even though the fundamental principles involved are exactly the same.

CHAPTER IX

ACIDIMETRY AND ALKALIMETRY

36. Equivalent Weights Applied to Acidimetry and Alkalimetry.—The fundamental reaction of Acidimetry and Alkalimetry is as follows:

$$H^+ + OH^- \rightarrow H_2O,$$

that is, the neutralization of an acid by a base, or the neutralization of a base by an acid. Standard solutions are required and calculations of analyses necessarily involve their concentrations. The definitions given in the preceding chapter are very easily applied to the solutions of this group, but a few simple illustrations will be of value.

When hydrochloric acid reacts as an acid, the gram-molecular weight (36.46 grams) of hydrogen chloride furnishes for the neutralization of any base, one gram-atom (1.008 grams) of reacting hydrogen. According to the definition, the value 36.46 grams constitutes the gram-equivalent weight of hydrogen chloride, and a liter of solution containing this amount is a normal solution of the acid. In this case, the normal solution and the molal solution are identical. On the other hand, the amount of hydrogen sulphate required to furnish in reaction one gram-atomic weight of hydrogen is only one-half the gram-molecular weight, or $\frac{H_2SO_4}{2} = 49.04$ grams, and a normal solution of sulphuric acid would contain 49.04 grams of hydrogen sulphate per liter of solution. A molal solution of sulphuric acid is therefore 2 normal, and contains 2 gram-equivalent weights per liter, or 2 gram-milliequivalent weights per cubic centimeter.

Acetic acid, $HC_2H_3O_2$, contains four hydrogen atoms in its molecule, but when the compound acts as an acid, only one of these hydrogens is involved in active reaction; thus,

$$HC_2H_3O_2 + NaOH \rightarrow NaC_2H_3O_2 + H_2O.$$

Consequently, $\frac{HC_2H_3O_2}{1} = 60.04$ grams of acetic acid constitutes the gram-equivalent weight, and the normal solution contains this weight of acid in a liter, or 0.06004 gram of acetic acid per cubic centimeter.

In regard to the bases, sodium hydroxide will serve as a simple illustration. This compound is neutralized as follows:

$$NaOH + H^+ \rightarrow H_2O + Na^+,$$

for example,

$$NaOH + HCl \rightarrow H_2O + NaCl.$$

$\frac{NaOH}{1}$ or 40.01 grams of sodium hydroxide constitutes one gram-equivalent weight of the alkali, not because the molecule *contains* one atom of hydrogen, but because it involves in reaction one atom of hydrogen, as shown in the above equations. Therefore 40.01 grams of sodium hydroxide in a liter of solution represents the normal solution. When calcium oxide is used as a base, each gram-molecule reacts with two gram-atoms of hydrogen:

$$CaO + 2H^+ \rightarrow Ca^{++} + H_2O,$$

or $\frac{CaO}{2} = 28.04$ grams of calcium oxide are needed to involve in reaction one gram-atom of hydrogen. Therefore, 28.04 grams of calcium oxide constitute the gram-equivalent weight in this case, although calcium oxide in itself *contains* no hydrogen whatever.

Problems

149. What is the equivalent weight of potassium hydroxide as a base?
Ans. 56.11.

150. What is the equivalent weight of $KHSO_4$ as an acid?
Ans. 136.2.

151. What is the milliequivalent weight in grams of each of the following acids or bases assuming complete neutralization in each case: (*a*) Na_2CO_3; (*b*) K_2O; (*c*) NH_4OH; (*d*) HBr; (*e*) H_2SO_3?

Ans. (*a*) 0.05300.
(*b*) 0.04710.
(*c*) 0.03505.
(*d*) 0.08093.
(*e*) 0.04104.

152. What is the equivalent weight of the following acids or bases assuming complete neutralization in each case: (*a*) N_2O_5; (*b*) $(NH_4)_2O$; (*c*) $Ba(OH)_2$; (*d*) NH_3; (*e*) SO_2?

Ans. (*a*) 54.01.
(*b*) 26.05.
(*c*) 85.70.
(*d*) 17.03.
(*e*) 32.03.

153. What is the gram-milliequivalent weight of K_2CO_3 in the reaction $K_2CO_3 + HCl \rightarrow KHCO_3 + KCl$? What is the gram-equivalent weight of H_3PO_4 in the reaction $H_3PO_4 + 2NaOH \rightarrow Na_2HPO_4 + 2H_2O$?

Ans. (*a*) 0.1382.
(*b*) 49.03.

154. How many grams of KOH are required to make (*a*) a liter of molal solution; (*b*) a liter of normal solution; (*c*) 400 c.c. of half-normal solution?

Ans. (*a*) 56.11 grams.
(*b*) 56.11 grams.
(*c*) 11.22 grams.

155. What is the normality of a nitric acid solution which is three molal? How many grams of HNO_3 are contained in 27.5 c.c. of 0.1070 N nitric acid?

Ans. 3N; 0.1854 gram.

156. What weight of CaO is necessary to prepare (*a*) 500 c.c. of a one-hundredth molal solution of $Ca(OH)_2$; (*b*) 30.63 c.c. of N/100 $Ca(OH)_2$?

Ans. (*a*) 0.2804 gram; (*b*) 0.008588 gram.

157. What is the normality of a sulphurous acid solution containing 6.32 grams of SO_2 per liter? Of an ammonium hydroxide solution containing 17.50 grams of NH_3 in 480 c.c. of solution?

Ans. 0.197 N. 2.14 N.

158. A solution of hydrochloric acid has a specific gravity of 1.200 and contains 39.11 per cent HCl by weight. Calculate (*a*) the molal concentration of the solution; (*b*) the normality of the solution; (*c*) the number of gram-equivalent weights of HCl in every 750 c.c. of solution.

Ans. (*a*) 12.87 molal; (*b*) 12.87 N; (*c*) 9.65.

159. A solution of sulphuric acid contains 0.1721 gram-equivalent weight of H_2SO_4 in a liter. What is the normal value of the solution? What is its molal value?

Ans. 0.1721 N; 0.08605 molal.

160. How much water must be added to 760 c.c. of a one-fourth molal barium hydroxide solution in order to prepare a tenth-normal solution? How many grams of $Ba(OH)_2.8H_2O$ must be dissolved and diluted to 400 c.c. to prepare at N/12 solution? How many moles per liter, and how many gram-equivalent weights per liter does this last solution contain?

Ans. 3040 c.c.
5.26 grams.
0.04167 mole.
0.08333 gram-equivalent weight.

161. How many cubic centimeters of nitric acid (sp. gr. 1.42, containing 69.80 per cent HNO_3 by weight) must be taken so that by dilution with water, 800 c.c. of N/2 acid may be prepared?

Ans. 25.4 c.c.

37. Ratio of Reacting Solutions.—Since a gram-equivalent weight of any acid is capable of *furnishing* exactly one gram-atom (1.008 grams) of active hydrogen, and since a gram-equivalent weight of any base is capable of *reacting with* exactly one gram-atom of hydrogen, it follows that (1) an equivalent weight of any acid must exactly neutralize an equivalent weight of any base; and (2) 1 liter of normal solution of any acid must exactly neutralize 1 liter of a normal solution of any base. More generally, a volume of any acid solution will be neutralized by an equal volume of any alkali solution of the same normal concentration.

If the reacting solutions of acid and base are of different concentrations, the relative volumes required for neutralization will be inversely proportional to the respective normalities. Thus, 50 c.c. of 4 normal acid will require 100 c.c. of 2 normal base for neutralization, for since the base is one-half as concentrated, twice the volume will be required.

Problems

162. How many cubic centimeters of normal sodium hydroxide solution are required to neutralize 5 c.c. of (*a*) N HCl, (*b*) N/2 HCl; (*c*) N/5 H_2SO_4; (*d*) N/5 HCl?

Ans. (*a*) 5 c.c.; (*b*) 2.5 c.c.; (*c*) 1 c.c.; (*d*) 1 c.c.

163. A solution of HCl contains 0.1243 equivalent of HCl per liter. How many cubic centimeters of normal KOH solution are necessary to neutralize 10.00 c.c. of the acid?

Ans. 1.243 c.c.

164. A solution of H_2SO_4 is 0.1372 normal. How many cubic centimeters of 0.1421 normal KOH solution are required to neutralize 13.72 c.c. of the acid?

Ans. 13.24 c.c.

165. Convert 42.95 c.c. of 0.1372 normal hydrochloric acid to the equivalent volume of normal solution.

Ans. 5.892 c.c.

166. Subtract 34.37 c.c. of 0.1972 HCl from 42.00 c.c. of N/5 HCl by converting both values to the equivalent volumes of normal acid. Express the answer in terms of (*a*) cubic centimeters of N HCl; (*b*) number of milliequivalents of HCl; (*c*) number of cubic centimeters of N/2 NaOH.

Ans. (*a*) 1.622 c.c.; (*b*) 1.622; (*c*) 3.244 c.c.

167. To neutralize 10.00 c.c. of dilute acetic acid 13.12 c.c. of 0.1078 N KOH were required. What was the normality of the acid?

Ans. 0.1415 N.

168. A solution containing 31.21 c.c. of N/10 HCl is added to a solution containing 98.53 c.c. of 0.5 N H_2SO_4, and 50.00 c.c. of 1.002 N KOH are added. Is the resulting solution acid or alkaline? How many cubic centimeters of N/3 acid or alkali will make it exactly neutral?

Ans. Acid; 6.85 c.c. of alkali.

169. Fifty cubic centimeters of 1.087 normal HCl are added to 28.00 cubic centimeters of a solution of a solid substance having an alkaline reaction. The alkali is more than neutralized. Ten cubic centimeters of 0.1021 N alkali were necessary to make the solution exactly neutral. How many milliequivalents of base per cubic centimeter did the original solution of solid substance contain, and what was its normality as an alkali?

Ans. 1.904; 1.904 N.

38. Adjusting Solutions to a Desired Normality.—A solution with a given normality is often found to be too concentrated or too dilute for the purpose for which it is to be used. In order to decrease its concentration, water is usually added; and in order to increase its concentration, a solution is added which contains the solute in greater concentration than the one given. The amounts required in each case may be determined by simple calculation.

EXAMPLE I.—How much water must be added to 750.0 c.c. of a 2.400 normal solution in order to make it 1.760 normal?

If the solution is 2.400 normal, it must contain 2.400 gram-equivalent weights of solute per liter, or $2.400 \times \frac{750.0}{1000} = 1.800$ gram-equivalent weights in 750 c.c. In order to be 1.760 normal, there must be 1.760 gram-equivalent weights of solute per liter, and therefore 1.800 gram-equivalent weights must be present in $\frac{1.800}{1.760} \times 1000 = 1023$ c.c. of solution. The 750 c.c. must be diluted to 1023 c.c., or $1023 - 750 = 273$ c.c. of water must be added. *Ans.*

With a given weight of solute, the normality of the solution will vary inversely with the solution volume. Hence, the same answer may be directly obtained from the simple ratio: $\frac{V_1}{V_2} = \frac{N_2}{N_1}$, in which V_1, N_1, V_2, and N_2 denote respectively the volume and normality of the undiluted and of the diluted solutions. Thus, $\frac{750}{V_2} = \frac{1.760}{2.400}$, whence $V_2 = 1023$, and the water added is equal to 1023 − 750, or 273 c.c. *Ans.*

EXAMPLE II.—How much 6 normal base must be added to 750.0 c.c. of a 2 normal base in order that the resulting solution shall be exactly 3 normal?

The 2 normal base must contain $2 \times \frac{750.0}{1000} = 1.500$ gram-equivalent weights of substance. Assume that x c.c. of 6 normal base are added. The total volume is $750.0 + x$ c.c., and since each cubic centimeter of 6 N base contains 0.006 gram-equivalents, the total number of gram-equivalent weights is $1.500 + 0.006x$. Each cubic centimeter of the mixture therefore contains $\frac{1.500 + 0.006x}{750.0 + x}$ gram-equivalent weights, and since the concentration of the resulting solution is given as 3 normal, this expression must equal 0.003, thus,

$$\frac{1.500 + 0.006x}{750.0 + x} = 0.003.$$

Solving, $x = 250.0$ c.c. *Ans.*

Problems

170. One cubic centimeter of a solution of sodium carbonate contains exactly 0.0109 gram of pure Na_2CO_3. To what volume must 100 c.c. of the solution be diluted to make it exactly N/100?

Ans. 2056 c.c.

171. A solution of sulphuric acid is standardized gravimetrically and it is found that 25.00 c.c. will precipitate 0.3059 gram of $BaSO_4$. To what volume must a liter of the acid be diluted in order to be exactly N/10?

Ans. 1047 c.c.

172. A solution of sodium hydroxide is found on analysis to be 0.5374 normal and a liter of it is available. How many c.c. of normal NaOH solution must be added in order to make the resulting solution 0.6000 normal?

Ans. 156.5 c.c.

173. What volumes of 3 N and 6 N hydrochloric acid must be mixed to make a liter of 5 N acid?

Ans. 666.7 c.c. 6 N.
333.3 c.c. 3 N.

174. What volume of 0.2063 N KOH must be added to 150.0 c.c. of 0.1320 N KOH in order that the resulting solution shall have the same basic strength as a solution which contains 15.50 grams of $Ba(OH)_2$ per liter?

Ans. 288.6 c.c.

39. Normality of a Solution Made by Mixing Similar Constituents.—When several similar constituents are mixed and dissolved in water, the normality of the resulting solution is determined by calculating the total number of equivalent weights present in a liter of solution, or by taking the sum of the normalities as figured for the individual solutions.

EXAMPLE I.—If 3.00 grams of solid KOH and 5.00 grams of solid NaOH are mixed, dissolved in water, and the solution made up to 1500 c.c., what is the normality of the solution as a base?

The number of equivalent weights of KOH in 1500 c.c. is $\frac{3.00}{\text{KOH}} = \frac{3.00}{56.11}$. In 1 liter there are $\frac{3.00}{56.11} \times \frac{1000}{1500} = 0.0356$ equivalent weight of KOH. In a liter of the solution there are also $\frac{5.00}{40.01} \times \frac{1000}{1500} = 0.0833$ equivalent weight of NaOH. A total of $0.0356 + 0.0833 = 0.1189$ equivalent weight of base in a liter makes the normality of the solution as a base 0.1189 N. *Ans.*

Or, since the solution contains $\frac{3.00}{1.5}$ grams of KOH per liter, its normality with respect to KOH is $\frac{3.00}{1.5} \div 56.11 = 0.0356$ N, and with respect to NaOH is $\frac{5.00}{1.5} \div 40.01 = 0.0833$ N. The sum of these values, 0.1189, represents the normality of the solution as a base. *Ans.*

Problems

175. In preparing an alkaline solution for use in volumetric work, an analyst because of shortage of chemicals dissolved exactly 48.17 grams of pure KOH and 36.21 grams of pure NaOH in water and diluted to 1200 c.c. What was the normality of the resulting solution as a base?

Ans. 1.469 N.

176. What is the normality of an alkali solution made by dissolving 6.73 grams of NaOH (99.5 per cent NaOH, 0.5 per cent H_2O) and 9.42 grams of pure $Ba(OH)_2.8H_2O$ in water and diluting to 850 c.c.?

Ans. 0.2672 N.

177. Fifty cubic centimeters of sulphuric acid (sp. gr. 1.42, containing 52.15 per cent of H_2SO_4 by weight) and 50 c.c. of sulphuric acid (sp. gr. 1.84, containing 95.60 per cent H_2SO_4 by weight) are mixed and diluted to 1500 c.c. What is the normal value of the solution as an acid?

Ans. 1.699 N.

178. If 50.00 c.c. of a solution containing 5 grams of NaOH are added to 50.00 c.c. of a solution containing 5 grams of KOH, what is the normality of the mixture before and after dilution to 116.3 c.c.?

Ans. 2.141 N.
1.841 N.

179. If a sample of NaOH contains 2 per cent by weight of Na_2CO_3 and 6 per cent by weight of H_2O, and 40.00 grams are dissolved in water and diluted to a liter, what is the normality of the resulting solution as a base? Assume complete neutralization.

Ans. 0.9351 N.

180. Fifty grams of a solid dibasic acid (molecular weight = 126) are mixed with 25 grams of a solid monobasic acid (molecular weight = 122). The mixture is dissolved and diluted to 2500 c.c. What is the normality of the solution as an acid?

Ans. 0.3995 N.

181. What is the normality as an acid of a solution made by mixing the following components? Assume no change in volume due to chemical effects.

(*a*) 160 c.c. of 0.3050 N HCl.
(*b*) 300 c.c. of half-molal H_2SO_4.
(*c*) 140 c.c. containing 1.621 grams of HCl.
(*d*) 200 c.c. containing 1.010 grams of H_2SO_4.

Ans. 0.5173 N.

40. Determination of the Normality of a Solution from Its Quantitative Preparation.—A solution may be standardized (*i.e.*, the normal value may be determined) in a variety of ways. In a few specific cases it is possible to prepare a standard solution by accurately weighing out the solute, dissolving, and diluting to a definite volume. This method is applicable only to solutions of such substances as can be weighed out accurately and the composition and purity of which are definitely known.

In some cases it is possible to determine the normality of a given solution by gravimetric methods; that is, by taking a defi-

nite volume of solution and precipitating the principal constituent in the form of a weighable compound of known composition. From the weight of this compound the weight of the solute in the volume of solution taken is calculated. This gives a direct measure of the normality. For example, if a certain volume of hydrochloric acid is treated with an excess of silver nitrate, the weight of the precipitated silver chloride is a measure of the weight of hydrogen chloride in a liter of the acid. Since a liter of normal hydrochloric acid contains 36.47 grams of HCl, the normal value of the solution is found by direct proportion.

41. Determination of the Normality of a Solution by Titration against a Solution of Known Concentration.—A normal solution contains one gram-equivalent of reactive substance per liter, or one gram-milliequivalent per cubic centimeter. A two-normal solution contains two milliequivalents per cubic centimeter. Three cubic centimeters of the latter contain $2 \times 3 = 6$ milliequivalents of reactive substance. That is, the product of the number of cubic centimeters of a solution and its normality equals the number of milliequivalents of dissolved substance, or

$$c.c. \times N = \textit{number of milliequivalents}$$

where *c.c.* is the volume in cubic centimeters and N is the normality. Therefore when two solutions react,

$$V_1N_1 = V_2N_2,$$

since the number of equivalents or milliequivalents of reacting substances must be the same.

A solution can therefore be standardized by determining what volume of it will exactly react with a definite volume of another solution the normality of which is already known. The normalities of the two solutions will then be in inverse ratio to the respective volumes used. Thus 50 c.c. of any half-normal acid will neutralize 50 c.c. of any half-normal base or 100 c.c. of quarter-normal base since the solutions contain the same number of equivalent weights of reacting substance (*i.e.* 25 gram-milliequivalents). To neutralize 60 c.c. of 0.5 N alkali solution (30 milliequivalents), 15 c.c. of 2 N acid (30 milliequivalents) will be required regardless of the chemical composition of the acid or alkali used. The chemical compositions of the reacting

substances are taken into account in preparing their standard solutions.

EXAMPLE I.—What is the normality of a solution of H_2SO_4 if 27.80 c.c. are required to neutralize a 25 c.c. pipetteful of 0.4820 N alkali?

$$25 \times 0.4820 = 12.05 \text{ milliequivalents.}$$

$$\frac{12.05}{27.80} = 0.4334 \text{ N.} \quad \textit{Ans.}$$

42. Determination of the Normality of a Solution by Titration against a Substance of Known Purity.—A solution is most often standardized by determining the exact volume of it required to react with a known weight of substance of *known* purity (usually, but not necessarily, 100 per cent pure). One liter of a normal solution of an acid, for example, contains one gram-equivalent weight of that acid and therefore must just neutralize one gram-equivalent weight of any base, or one cubic centimeter (a more convenient unit for ordinary experimental work) of the acid will neutralize one gram-milliequivalent weight of any base. One cubic centimeter of normal acid will just neutralize one milliequivalent weight in grams of any base. For example, it will neutralize $\frac{Na_2CO_3}{2{,}000} = 0.05303$ gram of pure sodium carbonate, $\frac{K_2CO_3}{2{,}000} = 0.06913$ gram of pure potassium carbonate, or $\frac{NaOH}{1{,}000} = 0.04001$ gram of pure sodium hydroxide. If 1 c.c. of an acid solution were found to neutralize 0.1061 gram (*i.e.*, two gram-milliequivalents) of pure sodium carbonate, the acid would be two normal. If 1 c.c. of an acid solution were found to neutralize 0.02001 gram (one-half gram-milliequivalent) of pure sodium hydroxide, the acid would be one-half normal. The same reasoning holds true for the standardization of alkali solutions against acids, and as will be seen later, for the standardization of solutions of oxidizing, reducing, and precipitating agents. In calculating the normal value of a solution standardized in this way, the number of grams of pure standardizing agent divided by its milliequivalent weight gives the number of gram-milliequivalents present. This must be the same as the number of gram-milliequivalents of substance in the solution

used. Since this equals the number of cubic centimeters times the normality,

$$c.c._s \times N_s = \frac{grams_x}{e_x}$$

or

$$N_s = \frac{grams_x}{c.c._s \times e_x}$$

where e_x is the milliequivalent weight of pure substance x which is titrated by solution s.

Example I.—A sample of pure oxalic acid ($H_2C_2O_4.2H_2O$) weighs 0.2000 gram, and requires exactly 30.12 c.c. of potassium hydroxide solution for complete neutralization. What is the normality of the KOH solution?

The milliequivalent weight of oxalic acid is

$$\frac{H_2C_2O_4.2H_2O}{2{,}000} = 0.06303.$$

The number of milliequivalents of oxalic acid present is $\frac{0.2000}{0.06303}$.

The number of milliequivalents of KOH required $= 30.12 \times N$.

$$30.12 \times N = \frac{0.2000}{0.06303}$$

$$N = 0.1053. \quad Ans.$$

Problems

182. A hydrochloric acid solution is of such strength that 45.62 c.c. are exactly equivalent to 1.600 grams of pure Na_2CO_3. Calculate (*a*) the number of gram-equivalents of Na_2CO_3 neutralized by 1 liter of the acid; (*b*) the number of gram-milliequivalents of Na_2CO_3 neutralized by 1 c.c. of the acid; (*c*) the normal value of the acid.

Ans. (*a*) 0.6616; (*b*) 0.6616; (*c*) 0.6616 N.

183. A 10-c.c. portion of dilute sulphuric acid was standardized gravimetrically by adding an excess of $BaCl_2$, filtering, igniting, and weighing the resulting precipitate. The weight was found to be 0.2762 gram. Calculate the normality of the acid.

Ans. 0.2366 N.

184. The normality of a sulphuric acid solution is 0.5278. If 38.61 c.c. of the acid are equivalent to 31.27 c.c. of a solution of NaOH, calculate the normality of the NaOH. If 38.61 c.c. of the acid are equivalent to 31.27 c.c. of a solution of $Ba(OH)_2$, what is the normality of the $Ba(OH)_2$?

Ans. 0.6516 N; 0.6516 N.

185. Calculate the normality of solution of hydrochloric acid and sodium hydroxide from the following data:

1 c.c. of HCl $\simeq$ 0.9492 c.c. of NaOH
39.81 c.c. of HCl $\simeq$ 0.6293 gram of AgCl

Ans. HCl = 0.1105 N.
NaOH = 0.1162 N.

186. A sample of pure $CaCO_3$ weighs 1.0000 gram and requires 40.10 c.c. of a solution of HCl for neutralization. What is the normal value of the acid? What volume of sulphuric acid of the same normality would be required for the same weight of $CaCO_3$? What volume of KOH solution of which 20 c.c. will neutralize 1.420 gram of KHC_2O_4 would be neutralized by 50.32 c.c. of the acid?

Ans. 0.4985 N; 40.10 c.c.; 45.26 c.c.

187. To a sample of sodium carbonate (99.20 per cent pure $Na_2CO)_3$ weighing 1.0500 grams are added 48.24 c.c. of a solution of acid which is in excess of the amount required for complete neutralization. The resulting solution is brought back to the neutral point with exactly 1.31 c.c. of sodium hydroxide solution of which 1.00 c.c. is equivalent to 1.01 c.c. of the acid. Calculate the normality of the acid.

Ans. 0.4189 N.

188. In standardizing an alkali against 0.1200 gram of a solid acid (equivalent weight = 114.7), 38.92 c.c. of the alkali are added before it is realized that the end point has been overstepped. By introducing 0.0050 gram of pure $H_2C_2O_4.2H_2O$ into the solution, it is found that 0.58 c.c. of the alkali is required to make the solution neutral. What is the normality of the alkali?

Ans. 0.02850 N.

189. A solution of sulphuric acid was standardized against calcium carbonate containing 91.90 per cent $CaCO_3$ and no other basic material. The sample weighing 0.7242 gram was titrated by adding an excess of acid (29.97 c.c.) and the excess was titrated with 10.27 c.c. of NaOH solution (1 c.c. of the acid $\simeq$ 1.024 c.c. of the NaOH). Calculate the normal value of each solution.

Ans. H_2SO_4 = 0.6664 N.
NaOH = 0.6507 N.

43. Calculation of Percentage Purity from Titration Values.—Just as the normal value of a solution can be found from the volume required to react with a definite weight of substance of known purity, the percentage purity of a substance can be determined from the volume of a solution of known normality required to react with a definite weight of the substance. For example, one cubic centimeter of normal alkali solution will neutralize one milliequivalent weight in grams of any acid.

If an acid is titrated with normal alkali, and exactly *two* cubic centimeters of the latter are required, it follows that *two* gram-milliequivalent weights of the acid must be present. If *two* cubic centimeters of *two* normal alkali are required, then *four* gram-milliequivalent weights of the acid must be present. In other words, the number of cubic centimeters multiplied by the normal value of the solution will give the number of milliequivalents (in grams) of substance reacted upon. The number of gram-milliequivalents thus found multiplied by the milliequivalent weight of the substance reacted upon will give the number of grams of that substance. If the percentage is desired, it is only necessary to divide this weight by the weight of sample taken and multiply by 100.

In general, therefore, if a substance x requires a certain number of *c.c.* of a solution s of normality N, and e is the milliequivalent weight of the substance,

$c.c._s \times N_s \times e_x = grams_x$ (compare formula of the preceding section)

and

$$\frac{c.c._s \times N_s \times e_x}{weight\ of\ sample} \times 100 = per\ cent_x$$

Example I.—A sample of soda ash (impure Na_2CO_3) is titrated with half-normal sulphuric acid. If the sample weighs 1.100 grams, and requires 35.00 c.c. of the acid for complete neutralization, what is the percentage of Na_2CO_3 in the ash, assuming no other active component to be present?

One cubic centimeter of normal acid will neutralize one gram-milliequivalent weight of any base. Thirty-five cubic centimeters of N/2 acid will neutralize $35.00 \times 0.5000 = 17.50$ gram-milliequivalent weights of any base. Since the milliequivalent weight of Na_2CO_3 is $\frac{Na_2CO_3}{2000} = 0.05301$, 35.00 c.c. of the N/2 sulphuric acid will react with

$$35.00 \times 0.5000 \times 0.05301 = 0.9276 \text{ gram of } Na_2CO_3.$$

As this weight is contained in a sample weighing 1.100 grams, the percentage of Na_2CO_3 in the sample is

$$\frac{0.9276}{1.100} \times 100 = 84.33 \text{ per cent.} \quad Ans.$$

It is important to remember that the normality of a solution merely expresses the ratio of its concentration to that of a solution containing one gram-equivalent weight of solute per liter (*i.e.*, a normal solution). Consequently, if the normality of a solution is known, the value of a definite volume of it in terms of other elements, compounds, or radicals can be found directly, even though the solution may not be capable of reacting directly with these elements, compounds, or radicals. Thus, the weight of hydrogen chloride in 10 c.c. of N/10 hydrochloric acid is

$$10 \times 0.1 \times \frac{HCl}{1{,}000} = 0.03647 \text{ gram.}$$

The weight of silver chloride precipitated by adding an excess of silver nitrate to 10 c.c. of N/10 hydrochloric acid is

$$10 \times 0.1 \times \frac{AgCl}{1{,}000} = 0.1433 \text{ gram.}$$

The weight of silver sulphate equivalent to the silver in the silver chloride precipitated by adding an excess of silver nitrate to 10 c.c. of N/10 hydrochloric acid is

$$10 \times 0.1 \times \frac{Ag_2SO_4}{2{,}000} = 0.1559 \text{ gram.}$$

The weight of barium in the barium sulphate obtained by adding an excess of barium chloride to the silver sulphate above is

$$10 \times 0.1 \times \frac{Ba}{2{,}000} = 0.06869 \text{ gram.}$$

In other words, as in the case of gravimetric computations, it is not necessary to calculate the weights of the intermediate products of a reaction. From the milliequivalent weight of the substance required, the weight of that substance may be determined directly.

EXAMPLE II.—Given the same conditions as in Example I, what would be the percentage of CO_2 in the soda ash?

$$35.00 \times 0.5000 = 17.50 \text{ gram-milliequivalents of } CO_2.$$

$$17.50 \times \frac{CO_2}{2{,}000} = 0.3850 \text{ gram of } CO_2.$$

$$\frac{0.3850}{1.100} \times 100 = 35.00 \text{ per cent } CO_2. \quad \textit{Ans.}$$

EXAMPLE III.—A 0.3000-gram sample of impure magnesium oxide is titrated with hydrochloric acid solution of which 3.00 c.c.

$\simeq$ 0.04503 gram $CaCO_3$. The end point is overstepped on the addition of 48.00 c.c. of the acid, and the solution becomes neutral upon the addition of 2.40 c.c. of 0.4000 N sodium hydroxide. What is the percentage of MgO in the sample?

$$1 \text{ c.c. HCl} \simeq \frac{0.04503}{3.00} \simeq 0.01501 \text{ gram of } CaCO_3.$$

$$\text{Normality of HCl} = \frac{0.01501}{\frac{CaCO_3}{2{,}000}} = 0.3000.$$

$$2.40 \text{ c.c. of } 0.4 \text{ N NaOH} \simeq 2.40 \times \frac{0.4000}{0.3000} \simeq 3.20 \text{ c.c. of } 0.3000 \text{ N HCl}$$

Net cubic centimeters of HCl used = 48.00 − 3.20 = 44.80 c.c.

44.80 × 0.3000 = cubic centimeters of N HCl = number of gram-milliequivalent weights of MgO.

$$44.80 \times 0.3000 \times \frac{MgO}{2{,}000} = \text{grams of MgO.}$$

$$\frac{44.80 \times 0.3000 \times \frac{40.32}{2{,}000}}{0.3000} \times 100 = 90.33 \text{ per cent MgO.} \quad \textit{Ans.}$$

Or

$$48.00 \times 0.3000 = 14.40 \quad \text{milliequivalents of HCl.}$$
$$2.40 \times 0.4000 = 0.96 \quad \text{milliequivalents of NaOH.}$$
$$14.40 - 0.96 = 13.44 = \text{net milliequivalents.}$$

$$\frac{13.44 \times \frac{MgO}{2{,}000}}{0.3000} \times 100 = 90.33 \text{ per cent MgO.} \quad \textit{Ans.}$$

Problems

190. Calculate the percentage of carbon dioxide in a sample of calcium carbonate from the following data. Total volume of N/2 HCl = 35.00 c.c.; total volume of N/10 NaOH = 17.50 c.c.; weight of sample = 1.000 gram.

Ans. 34.61 per cent.

191. Given the following data, calculate the percentage purity of a sample of cream of tartar ($KHC_4H_4O_6$):

Weight of sample = 2.527 grams; NaOH solution used = 25.87 c.c.; H_2SO_4 solution used = 1.27 c.c.; 1 c.c. of H_2SO_4 = 1.12 c.c. of NaOH; 1 c.c. of $H_2SO_4 \simeq$ 0.02940 gram $CaCO_3$.

Ans. 95.45 per cent.

192. Calculate the percentage of K_2CO_3 in a sample of pearl-ash from the following data:

Weight of sample = 2.020 grams; HCl used = 49.27 c.c.; NaOH used = 2.17 c.c.; 1 c.c. HCl = 0.02926 gram $CaCO_3$; NaOH = 0.3172 N.

Ans. 96.18 per cent.

193. A sample is known to be either pure KOH, pure NaOH, or a mixture of 50 per cent KOH and 50 per cent NaOH. A 1-gram sample is titrated with 0.5000 normal HCl and 50 c.c. are used. What is the composition of the substance?

Ans. Pure NaOH.

194. Given four 10-c.c. portions of 0.1000 normal hydrochloric acid solution. (*a*) How many grams of pure sodium carbonate will be neutralized by one portion? (*b*) How many grams of K_2O are contained in that weight of potassium hydroxide neutralized by another portion of the acid? (*c*) A sample of calcium carbonate is decomposed by a portion of the acid. Calculate the weight of $CaCO_3$ decomposed, the weight of CO_2 liberated, and the weight of $CaCl_2$ formed. (*d*) Calculate the weight of $KHC_2O_4.H_2C_2O_4.2H_2O$ equivalent in acid strength to a portion of the HCl.

Ans. (*a*) 0.05300 gram.
(*b*) 0.04710 gram.
(*c*) 0.05004 gram.
0.02200 gram.
0.05550 gram.
(*d*) 0.08473 gram.

195. Strong KOH will liberate NH_3 from ammonium salts. The liberated ammonia can be distilled and determined by absorbing it in standard acid and titrating the excess acid with standard alkali. From the following data calculate the percentage of NH_3 in a sample of impure ammonium salt.

Sample = 1.009 grams.
Standard acid used = 50.00 c.c. of 0.5127 N.
Standard alkali required = 1.37 c.c. of 0.5272 N.

Ans. 42.06 per cent.

196. Rochelle salt is $KNaC_4H_4O_6.4H_2O$ and on ignition is converted to $KNaCO_3$. The original sample of 0.9546 gram is ignited and the product titrated with sulphuric acid. From the data given, calculate the purity of the sample:

H_2SO_4 used = 41.72 c.c.
10.27 c.c. H_2SO_4 = 10.35 c.c. NaOH
NaOH = 0.1297 N.

NaOH used in titrating excess acid = 1.91 c.c.

Ans. 76.95 per cent.

197. A sample of zinc oxide is digested with 50.00 c.c. of normal sulphuric acid. The excess acid is titrated with 2.96 c.c. of 0.1372 normal alkali. The weight of sample is 2.020 grams. Calculate the percentage purity of the sample.

Ans. 99.89 per cent.

44. Problems in Which the Volume of Titrating Solution Bears a Given Relation to the Percentage of Constituent Present.—In commercial laboratories where many similar titrations are made each day, it is often convenient to simplify computation by taking each time for analysis a weight of sample such that the volume of standard solution used will bear some simple relation to the percentage of desired constituent. The advantages derived from such a procedure are the same as those discussed in Sec. 19, and the computations involved are similar in principle. In the volumetric problem it is also possible to fix the weight of sample and determine the normality of the titrating solution which must be used to fulfil a similar condition, although this type of problem is seldom met with in practice. It is far easier in practical work to vary a sample weight than it is to vary a solution concentration. In either case, however, the required weight of sample or normality of solution is best found by directly applying the formula previously derived, namely,

$$\frac{c.c._s \times N_s \times e_x}{weight\ of\ sample} \times 100 = per\ cent_x.$$

In this type of problem, it will always be found that of the five factors involved, two will be known, and a ratio will be given between two others, thus making possible the determination of the fifth factor.

EXAMPLE I.—What weight of soda ash should be taken for analysis such that the percentage of Na_2O present may be found by multiplying by 2 the number of cubic centimeters of N/5 acid solution used in the titration?

In any volumetric titration,

$$\frac{c.c._s \times N_s \times e_x}{weight\ of\ sample} \times 100 = per\ cent_x,$$

and in the problem given, N_s and e_x are known. A relation also exists between the *c.c.* and the *per cent* whereby

$$c.c. \times 2 = per\ cent.$$

Substituting,

$$\frac{c.c._s \times \frac{1}{5} \times \frac{Na_2O}{2{,}000}}{weight\ of\ sample} \times 100 = c.c._s \times 2$$

$$\frac{\frac{1}{5} \times \frac{62.00}{2{,}000}}{weight\ of\ sample} \times 100 = 2.$$

Weight of sample = 0.3100 gram. *Ans.*

The same precautions should be taken in solving this type of problem as were emphasized in the examples in Sec. 19, namely, that a numerical difference exists between a statement such as "the number of cubic centimeters is three times the per cent," and the statement "the per cent is found by multiplying the number of cubic centimeters by three." Thus, in the above example, the weight of soda ash to be taken so that *each cubic centimeter of N/5 acid shall equal one-half of* 1 *per cent* of Na_2O is found as follows:

$$\frac{1 \times \frac{1}{5} \times 0.03100}{weight\ of\ sample} \times 100 = \frac{1}{2}.$$

Weight of sample = 1.240 grams. *Ans.*

Problems

198. A sample of oxalic acid is to be analyzed by titrating with a solution of NaOH which is 0.1 N. What weight of sample should be taken so that each cubic centimeter of NaOH will represent one-half of 1 per cent of $H_2C_2O_4.2H_2O$?

Ans. 1.261 grams.

199. In the analysis of oxalic acid using a 1-gram sample, what must be the normality of the alkali used for titration so that the burette reading shall equal one-half the percentage of $H_2C_2O_4.2H_2O$?

Ans. 0.3173 N.

200. In the analysis of a sample of soda ash what weight of sample should be taken so that the volume in cubic centimeters of 0.4205 normal acid required for complete neutralization and the percentage of Na_2CO_3 in the sample shall be in the respective ratio of 8 to 17?

Ans. 1.049 grams.

201. A sample of a certain acid weighed 0.8250 gram and was titrated with N/5 alkali. After calculating the purity of the sample in terms of the percentage of constituent A, it was found that the percentage obtained was

just equal to the equivalent weight of A as an acid. What volume of titrating solution was used?

Ans. 41.25 c.c.

202. A sample of limestone is titrated for its value as a neutralizing agent. A 1-gram sample is always taken. What must be the normality of the titrating acid so that every 10 c.c. shall represent 4½ per cent of the neutralizing value expressed in terms of per cent CaO?

Ans. 0.1605 N.

203. Samples of pickling solution are to be analyzed volumetrically for acidity, and results are to be expressed in terms of cubic centimeters of H_2SO_4 (sp. gr. 1.84, containing 95.60 per cent H_2SO_4 by weight). The specific gravity of the pickling solution is 1.270 and a 25-c.c. pipetteful is taken for analysis. (*a*) What must be the normality of the standard alkali so that each cubic centimeter used shall represent 0.1 c.c. of the H_2SO_4? (*b*) So that every 10 c.c. shall represent 1 per cent of pure H_2SO_4?

Ans. (*a*) 3.588 N; (*b*) 0.6474 N.

204. What weight of soda ash must be taken for analysis so that by using 0.5 N HCl for titrating, (*a*) the burette reading shall equal the percentage of Na_2O; (*b*) three times the burette reading shall equal the percentage of Na_2O; (*c*) every 3 c.c. shall represent 1 per cent Na_2O; (*d*) each cubic centimeter shall represent 3 per cent Na_2O; (*e*) the burette reading and the percentage of Na_2O shall be in the respective ratio of 2 to 3?

Ans. (*a*) 1.550 grams.
(*b*) 0.5167 gram.
(*c*) 4.650 grams.
(*d*) 0.5167 gram.
(*e*) 1.033 grams.

45. Determination of Proportion in Which Components are Present in a Pure Mixture.—Indirect analyses in Volumetric Analysis are, in many cases, similar to those of Gravimetric Analysis, and methods of computing results should readily suggest themselves. Problems involving the determination from titration values of the proportion in which components are present in a pure mixture are identical in principle to the so-called "double chloride" problems of Gravimetric Analysis (see Sec. 21, Examples I and II), and the same algebraic method of solution may conveniently be used. The same type of analysis may be applied equally well to methods of oxidation and reduction.

EXAMPLE I.—Five-tenths of a gram of a mixture of calcium carbonate and barium carbonate require 30.00 c.c. of N/4 hydrochloric acid solution for neutralization. What is the percentage of each component?

Let x = number of grams of $CaCO_3$ in the mixture,
and y = number of grams of $BaCO_3$.
Then (1) $x + y = 0.5$.
Number of gram-milliequivalents of $CaCO_3$ present =

$$\frac{\frac{x}{CaCO_3}}{2{,}000} = \frac{x}{0.05004}.$$

Number of gram-milliequivalents of $BaCO_3$ present =

$$\frac{\frac{y}{BaCO_3}}{2{,}000} = \frac{y}{0.09869}.$$

Number of gram-milliequivalents of HCl used $= 30.00 \times \frac{1}{4}$.

Therefore (2) $\frac{x}{0.05004} + \frac{y}{0.09869} = 30.00 \times \frac{1}{4}$.

Solving equations (1) and (2) simultaneously,

$$x = 0.2471$$
$$y = 0.2529.$$

Percentage of $CaCO_3 = \frac{0.2471}{0.5000} \times 100 = 49.42$ per cent.

Percentage of $BaCO_3 = \frac{0.2529}{0.5000} \times 100 = 50.58$ per cent. *Ans.*

Problems

205. A mixture consisting entirely of lithium carbonate and barium carbonate weighs 1.000 grams and requires 15.00 c.c. of N HCl for neutralization. Calculate the percentage of $BaCO_3$ in the sample.

Ans. 71.24 per cent.

206. A mixture of pure lithium carbonate and pure strontium carbonate weighs 0.5280 gram and requires 19.82 c.c. of 0.5060 N acid for neutralization. What is the percentage of Li_2O and SrO in the sample?

Ans. Li_2O = 16.3 per cent.
SrO = 41.8 per cent.

207. What weight of barium carbonate must be added to 1 gram of lithium carbonate so that the mixture will require the same volume of standard acid for neutralization as would the same weight of pure calcium carbonate?

Ans. 0.716 gram.

208. A half-gram sample of a mixture of pure $CaCO_3$ and pure $SrCO_3$ requires 30.00 c.c. of 0.2726 N sulphuric acid for neutralization. (*a*) What

would be the loss in weight of the original sample on strong ignition? (*b*) Calculate the combined weight of $CaSO_4$ and $SrSO_4$ obtained above. (*c*) What is the weight of $CaCO_3$ in the original sample?

Ans. (*a*) 0.1799 gram; (*b*) 0.6473 gram; (*c*) 0.2176 gram.

209. The combined weight of LiOH, KOH, and $Ba(OH)_2$ in a mixture is 0.5000 gram and 25.44 c.c. of N/2 acid are required for neutralization. The same amount of material with CO_2 gives a precipitate of $BaCO_3$ which when filtered is found to require 5.27 c.c. of the above acid for neutralization. Calculate the weights of LiOH, KOH, and $Ba(OH)_2$ in the original sample.

Ans. LiOH = 0.2174 gram.
KOH = 0.0567 gram.
$Ba(OH)_2$ = 0.2259 gram.

46. Effect of the "Sensitiveness" of an Indicator on an Acidimetric Titration.—An indicator is used in Volumetric Analysis for the purpose of detecting the point at which a reaction is completed. The indicators used in acidimetry and alkalimetry are usually organic dyestuffs which are of one color in acid solution and of a distinctly different color in alkaline solution. They are usually in themselves either weak acids or weak bases, and the change in color which they undergo can be attributed to the fact that the arrangement of the atoms in their molecules is somewhat different from the arrangement of the atoms in the molecules of their corresponding salts. With a given concentration of indicator, the color change takes place at a point where the hydrogen-ion or the hydroxide-ion concentration in the solution has attained a definite value which is characteristic of the indicator in question. Thus, a solution containing about 0.001 per cent of phenolphthalein turns from colorless to pink when the hydroxide-ion concentration has attained the value of about 1×10^{-5} moles per liter, and the corresponding hydrogen-ion concentration has therefore been reduced to about 1×10^{-9} moles per liter (since in any solution at ordinary temperatures (H^+) (OH^-) = approximate 1×10^{-14}). Table VI in the Appendix gives the approximate hydrogen-ion and hydroxide-ion concentrations at which dilute solutions of the common indicators change color. From these data it will be seen that of the indicators given, phenolphthalein is the most sensitive to acids, and methyl orange and congo red are the most sensitive to bases.

Since in pure water at room temperature the concentration of the hydrogen ions and the concentration of the hydroxide ions

are each approximately 1×10^{-7} moles per liter, and since litmus is of an intermediate color at approximately this concentration, it might be concluded that litmus should be an ideal indicator for all titrations in acidimetry. It should be remembered that except in the titration of strong acids against strong bases forming unhydrolyzed salts, the exact completion of a neutralization titration is rarely in a strictly neutral solution. That is, when acid and alkali have been added in equivalent quantities, the resulting solution is frequently slightly acidic or slightly basic. Thus, when acetic acid is titrated with sodium hydroxide solution, sodium acetate and water are the products of the reaction:

$$HC_2H_3O_2 + NaOH \rightarrow NaC_2H_3O_2 + H_2O.$$

Sodium acetate, however, is somewhat hydrolyzed by water and tends to form a small amount of relatively un-ionized acetic acid, leaving an excess of hydroxide ions in the solution:

$$NaC_2H_3O_2 + H_2O \rightarrow Na^+ + OH^- + HC_2H_3O_2.$$

In other words, the reaction is appreciably reversible, and when the acid and base have been added in equivalent amounts, the solution is slightly alkaline. Hence, other conditions being equal, the correct indicator for a given titration is one of which the color change takes place when the solution has that hydrogen-ion or hydroxide-ion concentration which exists in a solution obtained by dissolving in the same volume of water the salt formed by the neutralization. With strong acids against strong bases, the sensitiveness of the indicator is of little importance since the salt formed is not hydrolyzed and a great change in the hydrogen-ion concentration of the solution is brought about by a very slight excess of titrating agent.

From suitable ionization constants it is possible to calculate the exact hydrogen-ion and hydroxide-ion concentration of a solution formed by adding exactly equivalent quantities of a given acid and a given base. Hence, it is possible to determine mathematically which indicator is theoretically best suited for a given titration.

Consider the titration of acetic acid with an equivalent quantity of sodium hydroxide, and the hydrolysis of the resulting salt as expressed by the second equation above. Since the unhydro-

lyzed salt can be considered as 100 per cent ionized into Na^+ and $C_2H_3O_2^-$ ions, the mass-action expression (see Chap. IV) for the hydrolysis becomes

$$\frac{(OH^-)(HC_2H_3O_2)}{(C_2H_3O_2^-)} = K.$$

This value is identical to that obtained by dividing the product $(H^+)(OH^-)$ by $\frac{(H^+)(C_2H_3O_2^-)}{(HC_2H_3O_2)}$, that is, the ion product of H_2O by the ionization constant of $HC_2H_3O_2$. The ion product $(H^+)(OH^-)$ at 25° is 1.0×10^{-14}. Therefore,

$$\frac{(OH^-)(HC_2H_3O_2)}{(C_2H_3O_2^-)} = \frac{1.0 \times 10^{-14}}{K_{HC_2H_3O_2}},$$

or in the titration of any weak monobasic acid, HX, by a strong base,

$$\frac{(OH^-)(HX)}{(X^-)} = \frac{1.0 \times 10^{-14}}{K_{HX}}.$$

It can be similarly shown that in the titration of any weak monoacidic base, XOH, with a strong acid,

$$\frac{(H^+)(XOH)}{(X^+)} = \frac{1.0 \times 10^{-14}}{K_{XOH}}.$$

Since in titrating a weak acid or a weak base it is customary to use a strong base or acid as a titrating solution, it is not necessary to consider the equilibrium conditions resulting from the hydrolysis of a salt of a weak base and a weak acid.

Example I.—The ionization constant of $HC_2H_3O_2$ is 1.8×10^{-5}. What is the hydrogen-ion concentration in a solution obtained by adding 40 c.c. of 0.1 N NaOH solution to 460 c.c. of water containing 40 c.c. of 0.1 N $HC_2H_3O_2$? Which of the common indicators is best suited for this titration?

$$\frac{(OH^-)(HC_2H_3O_2)}{(C_2H_3O_2^-)} = \frac{K_{H_2O}}{K_{HC_2H_3O_2}} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}$$

Let x = molal concentration of OH^- by hydrolysis of $NaC_2H_3O_2$.

Then x = molal concentration of un-ionized $HC_2H_3O_2$

and $0.008 - x$ = approximately 0.008 = molal concentration of unhydrolyzed $NaC_2H_3O_2$ and hence of $C_2H_3O_2^-$.

$$\frac{(x)(x)}{(0.008)} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}$$

$$x = 2.1 \times 10^{-6} = (OH^-)$$

Since in any solution $(H^+)(OH^-) = 1.0 \times 10^{-14}$

$(H^+) = 4.8 \times 10^{-9}$ moles per liter. *Ans.*

From Table VI (Appendix) it is seen that phenolphthalein is best suited as an indicator for the titration. *Ans.*

Problems

210. What is the approximate hydrogen-ion concentration of a solution which is colorless to phenolphthalein and blue to litmus?

Ans. 1×10^{-8}.

211. Would a hundredth molal solution of sodium bicarbonate be acid or alkaline to phenolphthalein? What would be the approximate H^+ ion concentration in such a solution?

Ans. Alkaline. 5.6×10^{-10}.

212. What volume of water must be added to 200 c.c. of 0.1 normal acetic acid in order that the resulting solution shall just give a blue color with congo red?

Ans. 160 c.c.

213. Fifteen grams of $NaC_2H_3O_2.3H_2O$ are dissolved in 500 c.c. of water and 500 c.c. of 0.1 N $HC_2H_3O_2$ are added. How would litmus, methyl orange, and methyl red behave toward the resulting solution? What is the H^+ ion concentration?

Ans. Pink; yellow; pink. 8.3×10^{-6}.

214. In an acidimetric titration 450 c.c. of a dilute ammonia solution require 50 c.c. of tenth normal HCl for neutralization. What should be the H^+ ion and the OH^- ion concentration at the end of an exact titration of the above? Which of the common indicators would be best suited for this titration?

Ans. 2.4×10^{-6}; 4.2×10^{-9}; methyl red.

215. If a solution of pure Na_2CO_3 is titrated with HCl using phenolphthalein, at the color change what per cent of the carbonate has not been converted to bicarbonate, and what per cent of the bicarbonate formed has been further reacted upon by the acid?

Ans. 0.3 per cent; 3.3 per cent.

216. Phenolphthalein is a weak organic acid which changes to pink when about one-third of it is neutralized. What is the ionization constant (=indicator constant) of phenolphthalein?

Ans. 5×10^{-10}.

47. Relation of the Equivalent Weight of an Acid or Base to the Indicator Used.—The fact that indicators exhibit different degrees of "sensitiveness" toward the detection of the end points of certain reactions must be considered in calculations

involving equivalent weights of acids and bases. Neutralization of a polybasic acid or of a polyacidic base takes place in steps whereby the reacting elements are replaced one at a time. Table VII (Appendix) shows at which stage of certain neutralization reactions the three common indicators change color, and these must be definitely known before a calculation from titration values can be made. When, for example, phosphoric acid, H_3PO_4, is gradually neutralized by a base, *e.g.*, NaOH, with methyl orange as an indicator, the color change takes place when only one hydrogen has been replaced to form NaH_2PO_4. With phenolphthalein as the indicator, the color change takes place when two hydrogens have been replaced. It follows therefore that the gram-equivalent weight of phosphoric acid is $\frac{H_3PO_4}{1} = 98.06$ grams when methyl orange is used for the indicator; it is $\frac{H_3PO_4}{2} = 49.03$ grams when phenolphthalein is used for the indicator; and it is $\frac{H_3PO_4}{3} = 32.69$ grams when the acid is completely neutralized, for in each case, that amount of acid involves in active reaction 1.008 grams of hydrogen.

Similarly, when sodium carbonate is gradually neutralized by an acid, with phenolphthalein as the indicator, the color change takes place in a cold solution when the carbonate has been converted into bicarbonate:

$$Na_2CO_3 + H^+ \rightarrow NaHCO_3 + Na^+.$$

With methyl orange, the color change takes place when all the carbonate has been neutralized:

$$Na_2CO_3 + 2H^+ \rightarrow CO_2 + H_2O + 2Na^+.$$

In the first reaction, the equivalent weight of sodium carbonate is $\frac{Na_2CO_3}{1} = 106.01$; in the second reaction, the equivalent weight is $\frac{Na_2CO_3}{2} = 53.00$.

48. Calculation of Analyses Involving the Use of Two Indicators.—The fact that certain indicators change color at different stages of a neutralization is sometimes made use of in volumetric work to determine the proportions of the components

of certain mixtures by making use of two end points in a single titration. This may be brought about by using two indicators, and the volumes of titrating solution required for the respective end points give a direct measure of the amounts of substances present. Only the two common indicators, methyl orange and phenolphthalein, will be considered.

Assume a solution to contain only sodium hydroxide and inert impurities. The weight of NaOH present may be found by direct titration with a standard solution of any strong acid, and with either methyl orange or phenolphthalein as the indicator. In either case, the color change will take place only when the alkali is completely neutralized, and the volume of standard acid used in the titration is a direct measure of the weight of NaOH present. If a solution contains only sodium carbonate and inert impurities and it is titrated with standard acid using methyl orange as the indicator, the color change takes place only when the Na_2CO_3 has been completely neutralized,

$$Na_2CO_3 + H^+ \rightarrow NaHCO_3 + Na^+$$
$$NaHCO_3 + H^+ \rightarrow Na^+ + H_2O + CO_2.$$

The volume of acid required is a measure of the total alkaline strength of the sample and of the actual weight of Na_2CO_3 present. In calculating, the equivalent weight of the Na_2CO_3 would be taken as one-half of the molecular weight. On the other hand, if phenolphthalein were used as the indicator and the titration were carried out in the cold, the color change from pink to colorless would occur when the carbonate had been changed to bicarbonate:

$$Na_2CO_3 + H^+ \rightarrow NaHCO_3 + Na^+.$$

The volume of standard acid required to titrate sodium carbonate to an end point with methyl orange as the indicator is twice that required if phenolphthalein is used as the indicator, since twice the number of hydrogen-ion equivalents are involved. The equivalent weight of the Na_2CO_3 is identical in the latter case to the whole molecular weight, $\frac{Na_2CO_3}{1}$, and the calculated weight of Na_2CO_3 present is the same in the two cases. It is important to note that if, with phenolphthalein as the indicator,

an *excess* of standard acid is added to the carbonate solution and *the carbon dioxide is expelled by boiling*, the sodium carbonate will be completely neutralized. Neutralization of the excess acid with standard alkali will give a *net* volume of acid which will be *the same* as that used with methyl orange as the indicator.

If a solution contains sodium bicarbonate and inactive impurities, the $NaHCO_3$ may be titrated with standard acid using methyl orange as the indicator or in *boiling solution* using phenolphthalein, in the latter case by adding excess acid and titrating back with alkali.

$$NaHCO_3 + H^+ \rightarrow Na^+ + H_2O + CO_2.$$

The equivalent weight of the $NaHCO_3$ in either case is identical to the molecular weight. As stated above, a *cold* solution of pure sodium bicarbonate gives no color with phenolphthalein and therefore cannot be titrated with phenolphthalein as the indicator.

There now remains the question of possible mixtures of the three alkalies just discussed. Altogether, there are the following theoretical possibilities:

(*a*) $NaOH$
(*b*) Na_2CO_3
(*c*) $NaHCO_3$
(*d*) $NaOH + Na_2CO_3$
(*e*) $Na_2CO_3 + NaHCO_3$
(*f*) $NaOH + NaHCO_3$
(*g*) $NaOH + Na_2CO_3 + NaHCO_3$.

Inert impurities may be present in each case. The last two mixtures, however, cannot exist in solution, for sodium hydroxide and sodium bicarbonate interact mole for mole to form the normal carbonate:

$$NaOH + NaHCO_3 \rightarrow Na_2CO_3 + H_2O.$$

Strictly speaking, these last two mixtures can exist when in the *perfectly dry* form, although this condition would be difficult to realize in practice. When treated with water the reaction takes place, forming the carbonate and leaving a possible *excess* of hydroxide or bicarbonate as the case may be. In solving problems involving these two dry mixtures, this reaction must be considered.

The mixtures ordinarily encountered in practice are those of (*d*) and (*e*), namely, sodium hydroxide with sodium carbonate, and sodium carbonate with sodium bicarbonate. Making use of two end points, it is possible to determine the proportions of the components of either of these mixtures even when inactive impurities are present.

EXAMPLE I. MIXTURE OF HYDROXIDE AND CARBONATE.—A 1.200-gram sample of a mixture of sodium hydroxide and sodium carbonate containing inert impurities is dissolved and titrated cold with half-normal hydrochloric acid solution. With phenolphthalein as an indicator, the solution turns colorless after the addition of 30.00 c.c. of the acid. Methyl orange is then added, and 5.00 c.c. more of the acid are required before this indicator changes color. What is the percentage of NaOH and of Na_2CO_3 in the sample?

If the acid is added slowly, the stronger base (NaOH) is neutralized first, as follows:

$$NaOH + HCl \rightarrow NaCl + H_2O.$$

After this reaction is complete, the carbonate is converted into bicarbonate:

$$Na_2CO_3 + HCl \rightarrow NaCl + NaHCO_3.$$

At this point, the phenolphthalein changes from pink to colorless, and a total of 30.00 c.c. of acid has been added. Then the bicarbonate formed is neutralized by 5.00 c.c. more of acid:

$$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2.$$

Since each mole of Na_2CO_3 reacts with 1 mole of HCl to give 1 mole of $NaHCO_3$, and this, in turn, is neutralized by 1 mole of HCl, it follows that in this particular mixture the volume of acid required to convert the Na_2CO_3 into $NaHCO_3$ is the same as the volume required to neutralize the $NaHCO_3$, namely, 5.00 c.c.

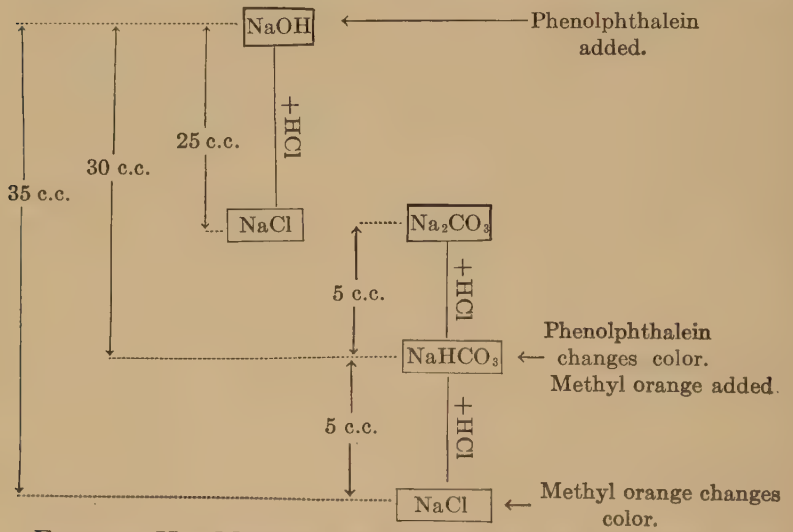
Therefore, the volume of acid necessary to neutralize completely the Na_2CO_3 is 10.00 c.c. Since the total volume added was 35.00 c.c., it is evident that 35.00 − 10.00 = 25.00 c.c. were necessary to neutralize the NaOH. Hence,

$$\text{Percentage of NaOH} = \frac{25.00 \times 0.5000 \times \frac{\text{NaOH}}{1{,}000}}{1.200} \times 100 = 41.68 \text{ per cent.}$$

$$\text{Percentage of } Na_2CO_3 = \frac{10.00 \times 0.5000 \times \frac{Na_2CO_3}{2{,}000}}{1.200} \times 100 = 22.08 \text{ per cent.}$$

Ans.

The volume relationships may be represented diagrammatically as follows:



EXAMPLE II.—MIXTURE OF CARBONATE AND BICARBONATE—A 1.200-gram sample of an impure mixture of sodium carbonate and sodium bicarbonate containing only inert impurities is dissolved and titrated cold with half-normal hydrochloric acid solution. With phenolphthalein as an indicator, the solution turns colorless after the addition of 15.00 c.c. of the acid. Methyl orange is then added, and 22.00 c.c. more of the acid are required to change the color of this indicator. What is the percentage of Na_2CO_3 and of $NaHCO_3$ in the sample?

When the acid is added slowly, the Na_2CO_3 is converted into $NaHCO_3$. At this point, the phenolphthalein changes color, and 15.00 c.c. of HCl have been added. As in Example I, the same volume of HCl would be required to convert this

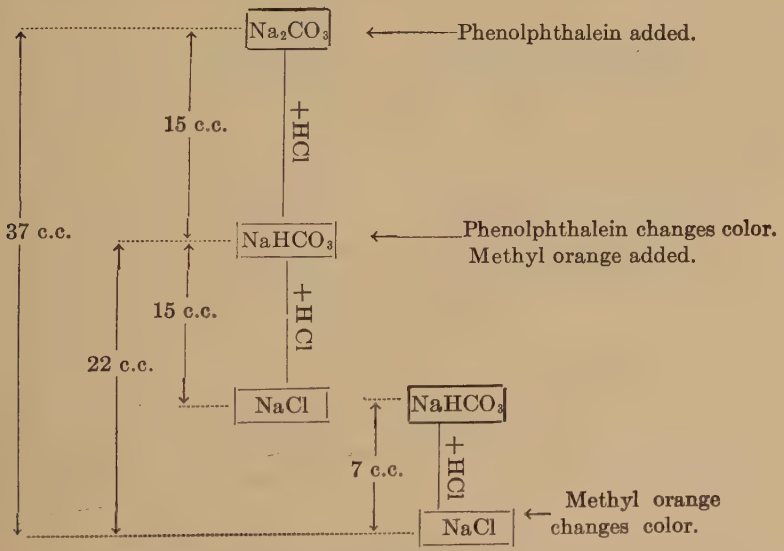
$NaHCO_3$ formed from the Na_2CO_3 into NaCl, H_2O, and CO_2 as was used for the conversion of the Na_2CO_3 into $NaHCO_3$. It follows that 15.00 + 15.00 = 30.00 c.c. of acid were required to neutralize completely the Na_2CO_3 present in the sample. The total volume being 15.00 + 22.00 = 37.00 c.c., it is evident that 37.00 − 30.00 = 7.00 c.c. of HCl were required to neutralize the $NaHCO_3$ present in the original sample. Hence,

$$\text{Percentage of } Na_2CO_3 = \frac{30.00 \times 0.5000 \times \frac{Na_2CO_3}{2{,}000}}{1.200} \times 100 = 66.25 \text{ per cent.}$$

$$\text{Percentage of } NaHCO_3 = \frac{7.00 \times 0.5000 \times \frac{NaHCO_3}{1{,}000}}{1.200} \times 100 = 24.50 \text{ per cent.}$$

Ans.

The volume relationships may be represented diagrammatically as follows:



In an analysis of the type discussed in this section, it is not always true that the analyst is previously aware of the exact composition of the sample. He may not know whether the sample contains hydroxide, carbonate, bicarbonate, or possible combinations of these components; and a qualitative test is

not always conclusive. By means of a simple titration, however, and the use of a double indicator or double end point, the composition of the alkali can be determined as far as these negative radicals are concerned.

A. The solution is titrated cold with phenolphthalein as the indicator. When the solution has just changed from pink to colorless (*i.e.*, has become slightly acid), methyl orange is added and a pink color is obtained (acid reaction). The alkalinity of the solution is due to *hydroxide.*

B. The solution is titrated cold with phenolphthalein as the indicator. When the pink color of the solution has just disappeared, methyl orange is added and the solution turns yellow. A volume of acid exactly equal to the volume used for the phenolphthalein end point is required to complete the titration (*i.e.*, change to pink). The alkalinity of the solution is due to *carbonate.*

C. The addition of phenolphthalein to the cold solution causes no color change, but when methyl orange is added, the solution turns yellow. The alkalinity of the solution is due to *bicarbonate.*

D. The volume of acid required to titrate the cold solution with phenolphthalein as the indicator is greater than the additional volume necessary to complete the titration with methyl orange as the indicator. The alkalinity is due to a mixture of *hydroxide and carbonate.*

E. The volume of acid required to titrate the cold solution with phenolphthalein as the indicator is less than the additional volume necessary to complete the titration with methyl orange as the indicator. The alkalinity is due to a mixture of *carbonate and bicarbonate.*

Problems

217. A sample of sodium carbonate containing sodium hydroxide and only inert impurities weighs 1.197 grams. It is dissolved and titrated in the cold with phenolphthalein as an indicator. The solution turns colorless when 48.16 c.c. of 0.2976 N HCl have been added. Methyl orange is added, and 24.08 c.c. more of the acid are required for complete neutralization. Calculate the percentages of NaOH and Na_2CO_3 in the sample.

Ans. NaOH = 23.95 per cent.
Na_2CO_3 = 63.46 per cent.

218. From the following data calculate the percentages of Na_2CO_3 and $NaHCO_3$ in a mixture in which they are the only alkaline components. Sample = 1.272 grams. Volume of 0.24 N HCl required for phenolphthal-

ein end point = 26.92 c.c. After adding an excess of the standard acid and boiling out the CO_2, the net additional volume of the acid required for the phenolphthalein end point = 50.21 c.c.

Ans. Na_2CO_3 = 53.84 per cent.
$NaHCO_3$ = 36.93 per cent.

219. A sample of material contains for its active components NaOH, Na_2CO_3, $NaHCO_3$ or possible mixtures of these. Two 1-gram samples are dissolved in water. To one sample, phenolphthalein is added and the solution is titrated cold with 1.038 N acid, requiring 17.96 c.c. The other sample is titrated cold with methyl orange as an indicator, and 21.17 c.c. of the same acid are required. What alkalies are present? Calculate the percentage of each.

Ans. NaOH = 61.28 per cent.
Na_2CO_3 = 35.31 per cent.

220. A chemist received different mixtures for analysis with the statement that they contained either NaOH, $NaHCO_3$, Na_2CO_3, or possible mixtures of these substances with inert material. From the data given, identify the respective materials and calculate the percentage of each component. One-gram samples and 0.2500 normal HCl were used in all cases.

Sample I.—Using phenolphthalein as an indicator, 24.32 c.c. were used. A duplicate sample required 48.64 c.c. with methyl orange as an indicator.

Sample II.—The addition of phenolphthalein caused no color change. With methyl orange, 38.47 c.c. of the acid were required.

Sample III.—15.29 c.c. of the acid were necessary to cause a color change in the cold with phenolphthalein, and an additional 33.19 c.c. were required for complete neutralization.

Sample IV.—The sample was titrated with acid until the pink of phenolphthalein disappeared, and required 39.96 c.c. On adding an excess of the acid, boiling, and titrating back with alkali, it was found that the alkali was exactly equivalent to the excess acid added.

Ans. I. 64.45 per cent Na_2CO_3; II. 80.79 per cent $NaHCO_3$; III. 40.52 per cent Na_2CO_3; 37.60 per cent $NaHCO_3$; IV. 39.97 per cent NaOH.

221. Equivalent weights of pure dry NaOH and pure dry $NaHCO_3$ were mixed. The resulting mixture weighed exactly 1 gram. This was dissolved in water. Calculate the number of cubic centimeters of 0.2513 N HCl required to titrate the solution when cold, using phenolphthalein as an indicator. After methyl orange is added what volume of the acid would be required?

Ans. 32.09 c.c.; 32.09 c.c.

222. Pure dry NaOH and pure dry $NaHCO_3$ are mixed in the respective proportion by weight of 2 to 1, and the mixture is dissolved in water. Calculate to three significant figures the ratio of the volume of standard acid required with phenolphthalein as an indicator, to the additional volume required with methyl orange.

Ans. 4.20.

223. Pure dry NaOH and pure dry $NaHCO_3$ are mixed in the respective proportion by weight of 1 to 2, and the mixture is dissolved in water. Calculate to three significant figures the ratio of the volume of standard acid required with phenolphthalein as an indicator, to the additional volume required with methyl orange.

Ans. 1.05.

224. A mixture which contains KOH and K_2CO_3 weighs a grams, and in the cold solution with phenolphthalein, requires b c.c. of c normal acid. After methyl orange is added, d c.c. of the acid are required. Calculate the percentage of KOH and of K_2CO_3. Reduce to simplest terms.

Ans. Per cent KOH $= \frac{5.611(b-d)c}{a}$; per cent $K_2CO_3 = \frac{13.82cd}{a}$.

225. Solve the above problem with respect to a mixture of Na_2CO_3 and $NaHCO_3$. Reduce to simplest terms.

Ans. Per cent $Na_2CO_3 = \frac{10.60\,bc}{a}$; per cent $NaHCO_3 = \frac{8.401(d-b)c.}{a}$.

49. Double Indicator Problems Applied to Titrations with Mixed Alkali Solutions.—When sodium or potassium hydroxide solutions are prepared as standard alkalies in volumetric work, it is customary to dissolve the solid sticks of the caustic in water and dilute the solution to the approximate volume required. Even when the so-called "chemically pure" solids are used, it is highly probable that they have been exposed to the air sufficiently to unite with an appreciable amount of carbon dioxide and thereby have become contaminated with sodium carbonate or potassium carbonate as the case may be. Under these conditions, the titrating solution contains, for example, NaOH and Na_2CO_3, and when used to titrate an acid, the volume required will depend upon the indicator used. When methyl orange is used, the total alkaline strength of the solution is effective in neutralizing the acid; with phenolphthalein, all the hydroxide and only one-half the carbonate is utilized before the color change takes place. This means that in titrating the same quantity of acid, a greater volume of the alkali solution would be required when phenolphthalein is used than when methyl orange is used as the indicator. In other words, the same principles discussed in the preceding section are involved in this case, but in the opposite way.

Example I.—An alkali solution is made up by dissolving in water solid sticks of NaOH which contain 3 per cent by weight of Na_2CO_3. If 40.00 c.c. of this solution are required to neu-

tralize a certain weight of strong acid with methyl orange as the indicator, what volume would be required for the same weight of acid if phenolphthalein were used?

The alkali solution contains three parts by weight of Na_2CO_3 to every 97 parts by weight of NaOH. It therefore contains $\frac{97}{\text{NaOH}} = \frac{97}{40.01} = 2.424$ equivalent weights of NaOH to every $\frac{3}{\frac{\text{Na}_2\text{CO}_3}{2}} = \frac{3}{53.00} = 0.05660$ equivalent weights of Na_2CO_3, considering the latter to be completely neutralized. It contains $\frac{97}{40.01} = 2.424$ equivalent weights of NaOH to $\frac{3}{\text{Na}_2\text{CO}_3} = \frac{3}{106.01} = 0.02830$ equivalent weights of Na_2CO_3 if the latter is half neutralized. The total number of equivalent weights in the former case is $2.424 + 0.05660 = 2.481$; the total number of equivalent weights in the latter case is $2.424 + 0.02830 = 2.452$. To furnish the same number of equivalent weights, that is, to neutralize the same quantity of given acid, volumes of the solution in the respective ratio of 2.452 to 2.481 must be taken. In other words, in the problem given, if 40.00 c.c. of the alkali were used with methyl orange as the indicator (*i.e.*, with the alkaline strength of the solution completely utilized), $40.00 \times \frac{2.481}{2.452} = 40.48$ c.c. would be required with phenolphthalein as the indicator. *Ans.*

Example II.—What are the relative proportions by weight of KOH and K_2CO_3 in a solution containing only these alkalies, if 31.00 c.c. of the solution are required to neutralize a certain volume of N/5 acid in the cold using phenolphthalein as an indicator, and 30.00 c.c. are required for the same volume of acid using methyl orange?

In principle this is the reverse of the preceding example. In this case, the number of equivalent weights of reacting base in the two instances are in the ratio of 30.00 to 31.00. Assume the alkali solution to contain KOH and K_2CO_3 in the respective

ratio by weight of x to y. Then there are $\frac{x}{\text{KOH}} = \frac{x}{56.11}$ equivalent weights of KOH, to $\frac{y}{\frac{\text{K}_2\text{CO}_3}{2}} = \frac{y}{69.10}$ equivalent weights of K_2CO_3 when the latter is completely neutralized (methyl orange), or $\frac{y}{138.21}$ equivalent weights when the latter is half neutralized (phenolphthalein). Then

$$\frac{\frac{x}{56.11} + \frac{y}{138.21}}{\frac{x}{56.11} + \frac{y}{69.10}} = \frac{30.00}{31.00}$$

Solving, $\frac{x}{y} = 11.77$

Therefore $KOH : K_2CO_3 = 11.77 : 1$. *Ans.*

Problems

226. A liter of an alkali solution is prepared from 38.00 grams of pure NaOH and 2.00 grams of pure Na_2CO_3. What is the true normality of the solution if completely neutralized? If this solution were used in a titration in the cold with phenolphthalein as an indicator what normality should be taken for the alkali?

Ans. 0.9874 N; 0.9686 N.

227. A solution made from KOH which it is known has been exposed to the air, and therefore contains K_2CO_3, is titrated against standard sulphuric acid (1 c.c. of the $H_2SO_4 \doteq 0.02335$ gram of $BaSO_4$). In titrating, the following data were obtained:

50.00 c.c. $H_2SO_4 \doteq 49.94$ c.c. alkali (phenolphthalein, cold)
50.00 c.c. $H_2SO_4 \doteq 49.37$ c.c. alkali (methyl orange)

Calculate the normality of the alkali if completely neutralized. Calculate the number of grams of KOH and K_2CO_3 per liter of solution.

Ans. 0.2026 N; 11.08 grams KOH, 0.33 gram K_2CO_3.

228. A sample of NaOH containing Na_2CO_3 and moisture is used to prepare a standard alkali. If 41.20 c.c. are required to neutralize 60.00 c.c. of N/3 acid (cold) with phenolphthalein as the indicator, and 10.00 c.c. are required to neutralize 15.00 c.c. of the acid with methyl orange as the indicator, (*a*) what are the proportions by weight of NaOH and Na_2CO_3 in the alkali solution; (*b*) how many grams of Na_2CO_3 are contained in each cubic centimeter of the alkali; (*c*) what volume of the alkali would be necessary to neutralize 0.2000 gram of $H_2C_2O_4.2H_2O$ if phenolphthalein were

used as an indicator and the alkali added slowly to the boiling hot solution?

Ans. (*a*) $\frac{NaOH}{Na_2CO_3} = 12.1$; (*b*) 0.00155 gram; (*c*) 6.35 c.c.

229. A solution of NaOH contaminated with Na_2CO_3 is standardized against a strong acid and with phenolphthalein in the cold is calculated to be 0.1267 N. With methyl orange, the solution is found to be actually 0.1272 N. Calculate the number of gram-equivalent weights of NaOH and of Na_2CO_3 per liter of solution.

Ans. NaOH = 0.1262; Na_2CO_3 = 0.0010.

230. Potassium hydroxide containing 2.20 per cent K_2CO_3 and 10.30 per cent H_2O is purchased at 58 cts. per pound. It is used in a certain process as a neutralizing agent for sulphuric acid, and the test for neutrality is made by adding phenolphthalein to the cold solution. Calculate (*a*) the cost for the neutralization of a gram-equivalent of H_2SO_4; (*b*) the cost per gram-equivalent of H_2SO_4 if methyl orange had been used as the indicator; (*c*) the neutralization cost per gram-equivalent of H_2SO_4 by the most economical method if solid NaOH containing 10 per cent Na_2CO_3 and 2 per cent H_2O may be purchased for 42 cts. per pound.

Ans. (*a*) 8.119 cts.
(*b*) 8.037 cts.
(*c*) 3.876 cts.

50. Titration of Acid Mixtures.—No set rules can be formulated for solving problems involving titrations of acid mixtures, because the procedures used depend upon the number and character of the components present. In general, the method of analysis allows the formulation of as many algebraic equations as there are unknown components in the mixture.

For example, a mixture of the components *W*, *X*, *Y*, and *Z*, of which *W* is a volatile acid (*e.g.*, HCl, HNO_3), *X* is a non-volatile acid (*e.g.*, H_2SO_4, H_3PO_4), *Y* is a volatile reducing acid (*e.g.*, SO_2, N_2O_3), and *Z* is water, may be analyzed in the following simple manner: (1) A weighed sample is titrated with a standard oxidizing agent and *Y* is determined. (2) A weighed sample is evaporated on the water bath and the residue *X* is determined by titration with standard alkali. (3) A weighed sample is titrated directly with standard alkali. After *X* and *Y* have been determined, the volume of alkali solution required for *X* and *Y* may be calculated. The volume of alkali used in direct titration minus the sum of the volumes used for *X* and *Y* represents the volume required for *W*, from which the percentage of *W* may be calculated. The percentage of *Z* is found by difference.

51. Special Cases of Acid Mixtures. Case A.—An important titration is that involved in the analysis of fuming sulphuric acid (oleum). This substance may be considered to be a solution of sulphur trioxide, SO_3, in hydrogen sulphate, H_2SO_4, and when no other component is present, the analysis is made by dissolving a weighed sample in water and titrating with standard alkali.

EXAMPLE I.—A sample of fuming sulphuric acid weighing 1.000 gram when dissolved in water requires 21.41 c.c. of N/1 NaOH solution for neutralization. What is the percentage of each component?

Method I.—Since fuming sulphuric acid is a mixture of two pure components, it is possible to solve the problem by a method similar to that described under the titration of a mixture of two pure bases (Sec. 45). Let x equal the weight of SO_3, and y the weight of H_2SO_4.

$$x + y = 1.000$$

$$\frac{x}{\frac{SO_3}{2{,}000}} + \frac{y}{\frac{H_2SO_4}{2{,}000}} = 21.41 \times 1.$$

Solving the simultaneous equations,

$$\left.\begin{array}{l} x = 0.2217 \text{ gram.} \quad \text{Per cent} \quad SO_3 = 22.17 \\ y = 0.7783 \text{ gram.} \quad \text{Per cent } H_2SO_4 = 77.83 \end{array}\right\} Ans.$$

The disadvantage of this method lies in the fact that its precision is relatively low, especially since the molecular weights of SO_3 and H_2SO_4 are nearly alike. The following method is much to be preferred:

Method II.—In dissolving the oleum, the SO_3 unites with water to form H_2SO_4:

$$SO_3 + H_2O \rightarrow H_2SO_4,$$

and the solution now contains only H_2SO_4 and H_2O.

$$\frac{21.41 \times 1 \times \frac{SO_3}{2{,}000}}{1.000} \times 100 = \text{percentage of total } SO_3 \text{ (combined and free) in the original mixture} = 85.70 \text{ per cent.}$$

Since the original mixture consisted of free SO_3, combined SO_3, and combined H_2O, 100.00 − 85.70 = percentage of combined H_2O in the original mixture = 14.30 per cent.

$$\text{Percentage of } H_2SO_4 \text{ in the mixture} = 14.30 \times \frac{H_2SO_4}{H_2O}$$

$$= 77.83 \text{ per cent}$$

$$\text{Percentage of } SO_3 = 100.00 - 77.83 = 22.17 \text{ per cent} \Big\} \textit{Ans.}$$

Method III.—This method of solution is interesting because of its simplicity, but Method II is preferred because of greater precision.

In dissolving the oleum, the SO_3 unites with part of the water to form H_2SO_4. If the total percentage of acid is computed in terms of H_2SO_4, the following result is obtained:

$$\frac{21.41 \times 1 \times \frac{H_2SO_4}{2{,}000}}{1.000} \times 100 = 105.0 \text{ per cent.}$$

Since in the original mixture $SO_3 + H_2SO_4 = 100.00$ per cent, the difference of 5.0 per cent is caused by the water which has combined with the SO_3. The SO_3 and H_2O combine mole for mole.

$$5.0 \times \frac{SO_3}{H_2O} = \text{percentage of } SO_3$$

$$= 22.2 \text{ per cent } SO_3$$

$$100.0 - 22.2 = 77.8 \text{ per cent } H_2SO_4 \Big\} \textit{Ans.}$$

Case B.—Fuming sulphuric acid often contains small amounts of SO_2 which with water forms H_2SO_3, and is included in the alkali titration:

$$H_2SO_3 + 2NaOH \rightarrow Na_2SO_3 + 2H_2O.$$

This is when phenolphthalein is used as the indicator. With methyl orange, the color change takes place at the bisulphite stage:

$$H_2SO_3 + NaOH \rightarrow NaHSO_3 + H_2O.$$

In case SO_2 is present, its amount is usually determined in a separate sample by titration with a standard oxidizing agent, and the other components are then computed from the alkali titration values in the usual way, with a correction for the volume of alkali used by the SO_2.

EXAMPLE I.—A sample of fuming sulphuric acid containing H_2SO_4, SO_3, and SO_2 weighs 1.000 gram and is found to require

23.47 c.c. of N/1 alkali for neutralization (phenolphthalein as indicator). A separate sample shows the presence of 1.50 per cent SO_2. Find the percentages of SO_3 and H_2SO_4.

$$\text{Volume of alkali used by } SO_2 = \frac{0.0150}{1 \times \frac{SO_2}{2{,}000}} = 0.47 \text{ c.c.}$$

Volume of alkali used for $H_2SO_4 + SO_3$

$$23.47 - 0.47 = 23.00 \text{ c.c.}$$

Percentage of $H_2SO_4 + SO_3 = 100.00 - 1.50 = 98.50$ per cent.

Following Method II above:

$$23.00 \times 1 \times \frac{\frac{SO_3}{2{,}000}}{1.000} \times 100 = 92.07 \text{ per cent total } SO_3$$

$$98.50 - 92.07 = 6.43 \text{ per cent combined } H_2O$$

$$\left.\begin{aligned} 6.43 \times \frac{H_2SO_4}{H_2O} &= 35.01 \text{ per cent } H_2SO_4 \\ 98.50 - 35.01 &= 63.49 \text{ per cent } SO_3 \end{aligned}\right\} Ans.$$

Problems

231. A sample of fuming sulphuric acid, containing no SO_2 or other impurity, on titration is found to contain 108.5 per cent acid expressed in terms of H_2SO_4. Calculate the percentage of free SO_3 in the sample.

Ans. 37.80 per cent.

232. A sample of fuming sulphuric acid containing only SO_3 and H_2SO_4 is titrated, and the percentage of total SO_3 (free and combined) is found to be 84.00 per cent. What is the percentage of H_2SO_4 in the original sample?

Ans. 87.08 per cent.

233. A sample of fuming sulphuric acid containing only SO_3 and H_2SO_4 weighs 1.4000 grams and requires 36.10 c.c. of 0.8050 normal NaOH for neutralization. What is the percentage of each constituent in the sample?

Ans. 91.98 per cent H_2SO_4.
8.02 per cent SO_3.

234. A solution of SO_3 in H_2SO_4 requires 65.10 c.c. of 0.9000 normal alkali for the titration of a sample weighing 2.604 grams. What is the proportion by weight of free SO_3 to H_2SO_4 in the sample?

Ans. 0.8497.

235. A sample of fuming sulphuric acid consisting of a solution of SO_3 and SO_2 in H_2SO_4 is found to contain 2.06 per cent SO_2. A sample weighing 1.500 grams requires 21.64 c.c. of 1.5 N KOH when phenolphthalein is used as the indicator. What are the percentages of free SO_3 and H_2SO_4 in the sample?

Ans. 22.38 per cent free SO_3.
75.56 per cent H_2SO_4.

CHAPTER X

OXIDATION AND REDUCTION METHODS

52. Fundamental Principles.—This phase of Volumetric Analysis has to do with the titration of an oxidizing agent with a standard solution of a reducing agent, or the titration of a reducing agent with a standard solution of an oxidizing agent. This type of determination embraces the greater part of Volumetric Analysis, for the number of substances capable of oxidation or reduction is comparatively large.

Oxidation is the increase in positive valence of an element or radical; reduction is the decrease in positive valence of an element or radical. Oxidation and reduction must evidently take place simultaneously, for in any reaction of this type the oxidizing agent is always reduced and the reducing agent is always oxidized, and to the same degree. The methods of expressing concentration and the definitions given in Chap. VIII hold true in every way for solutions of oxidizing and reducing agents. Therefore, the relationships existing between these agents are exactly the same as those existing between acids and bases. It is only necessary in the case of concentrations of solutions expressed in terms of the normal value to consider the hydrogen equivalent from a slightly different point of view.

53. Equivalent Weights of Oxidizing and Reducing Agents.—As in acidimetry and alkalimetry the concentration of a solution of an oxidizing or reducing agent is best expressed in terms of its relation to the normal solution, and the gram-atom of hydrogen is taken as the ultimate unit. Since the valence of hydrogen can change only one, it follows that as many hydrogen equivalents will be required to reduce a given substance as the number of units by which that substance changes in valence.

Consider the reduction of ferric chloride to ferrous chloride according to the hypothetical reaction:

$$2FeCl_3 + 2H \rightarrow 2FeCl_2 + 2HCl,$$

or

$$Fe^{+++} + H \rightarrow Fe^{++} + H^{+}.$$

One gram-atomic weight of hydrogen (or its equivalent in any other reducing agent) is necessary to decrease the valence of the iron in one mole of ferric chloride by one, or from "ferric" to "ferrous." Conversely, to oxidize one mole of ferrous chloride would involve the equivalent of one-half a gram-atomic weight of oxygen which in turn is equivalent to one gram-atomic weight of hydrogen:

$$FeCl_2 + \tfrac{1}{2}O + HCl \rightarrow FeCl_3 + \tfrac{1}{2}H_2O$$

or

$$Fe^{++} + \tfrac{1}{2}O + H^+ \rightarrow Fe^{+++} + \tfrac{1}{2}H_2O.$$

The reduction of a mole of stannic chloride to stannous chloride (valence change = 2) involves two gram-atomic weights of hydrogen or their equivalent:

$$SnCl_4 + 2H \rightarrow SnCl_2 + 2HCl \text{ (hypothetical)},$$

and to oxidize one mole of stannous chloride would involve the equivalent of one gram-atomic weight of oxygen (equivalent to two gram-atomic weights of hydrogen):

$$SnCl_2 + O + 2HCl \rightarrow SnCl_4 + H_2O \text{ (hypothetical)}$$

or

$$Sn^{++} + O + 2H^+ \rightarrow Sn^{++++} + H_2O.$$

As has been pointed out in gravimetric computation (see Sec. 16) for purposes of calculation the exact mechanism of a reaction is usually unimportant as long as the initial and final products are known. In the case of the oxidation of stannous chloride, the hypothetical equation just written serves the purpose of determining the equivalent weight of stannic chloride as well as an equation representing an actual reaction. Stannous chloride can be oxidized by mercuric chloride:

$$SnCl_2 + 2HgCl_2 \rightarrow SnCl_4 + Hg_2Cl_2,$$

but in this reaction each molecule of mercuric chloride is equivalent to an atom of hydrogen:

$$2HgCl_2 + 2H \rightarrow Hg_2Cl_2 + 2HCl,$$

or

$$Hg^{++} + H \rightarrow Hg^{+} + H^{+}.$$

As before, two hydrogen equivalents are necessary to convert stannous chloride to stannic chloride.

From fundamental definitions (see Chap. VIII), it is evident that the equivalent weights of ferric chloride and ferrous chloride

in oxidation and reduction reactions are $\frac{FeCl_3}{1} = 162.22$, and $\frac{FeCl_2}{1} = 126.76$ respectively; and the equivalent weights of stannic chloride and stannous chloride are $\frac{SnCl_4}{2} = 130.3$, and $\frac{SnCl_2}{2} = 94.85$ respectively. Similarly, the equivalent weight of the iron in the ferrous chloride or ferric chloride is $\frac{Fe}{1} = 55.84$; and the equivalent weight of the tin in the stannous chloride or stannic chloride is $\frac{Sn}{2} = 59.35$.

In general, the equivalent weight of an oxidizing agent involved in a given reaction may be found by either of the following methods:

A. By dividing the atomic or molecular weight of the element or compound by the total *change* in valence which it undergoes in the reaction involved.

B. By finding the amount of the substance which will be reduced to the same degree, either actually or hypothetically, by one atomic weight of hydrogen.

The equivalent weight of a reducing agent may be found:

A. By dividing the atomic or molecular weight of the element or compound by the total *change* in valence which it undergoes in the reaction involved.

B. By finding the amount of the substance which will be oxidized to the same degree, either actually or hypothetically, by one-half an atomic weight of oxygen (which is equivalent to one atomic weight of hydrogen).

A table showing the changes in valence of many elements and radicals in reactions commonly encountered in volumetric analyses has been included in Sec. 7, and should be consulted at this point. A few specific cases are discussed in greater detail below in order to emphasize the fundamental principles underlying calculations involved in this important field of analysis.

EXAMPLE I. POTASSIUM PERMANGANATE.—When potassium permanganate or any permanganate reacts as an oxidizing agent in acid solution, the manganese is reduced to the manganous state:

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \rightarrow 2MnSO_4 + 5Fe_2(SO_4)_3 + K_2SO_4 + 8H_2O.$$

Method A.—Since the manganese is reduced from a valence of +7 to a valence of +2, the equivalent weight of potassium permanganate in this reaction is $\frac{KMnO_4}{5} = 31.61$.

Method B.—If the same reduction is assumed to be brought about by hydrogen,

$$2KMnO_4 + 10H + 3H_2SO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 8H_2O,$$

it is seen that the amount of potassium permanganate which will react with one atomic weight of hydrogen is $\frac{2KMnO_4}{10} = 31.61$. When used in acid solution as an oxidizing agent, a liter of normal potassium permanganate solution therefore contains 31.61 grams of the pure salt.

When potassium permanganate is used as an oxidizing agent in *neutral* or *alkaline* solution, the reduction goes only to form manganese dioxide:

$$2KMnO_4 + 3MnSO_4 + 2H_2O \rightarrow 5MnO_2 + 2KHSO_4 + H_2SO_4.$$

The change in valence of the manganese in this case being 3, the equivalent weight is $\frac{KMnO_4}{3} = 52.66$. This is also evident from the hypothetical equation:

$$MnO_4^- + 3H \rightarrow MnO_2 + OH^- + H_2O.$$

It is obvious that the normality of a permanganate solution which has been standardized in acid solution cannot enter into calculation where the permanganate is used in neutral or basic solution unless correction is made for the difference in oxidizing power. In neutral or basic solution, permanganate is only *three-fifths as strong* as when used in the presence of acid.

Example II. Potassium Dichromate.—When a dichromate is reduced in acid solution, the valence of the chromium atom is changed from six to three:

$$K_2Cr_2O_7 + 6FeCl_2 + 14HCl \rightarrow 2CrCl_3 + 6FeCl_3 + 2KCl + 7H_2O,$$

or $Cr_2O_7^= + 6Fe^{++} + 14H^+ \rightarrow 2Cr^{+++} + 6Fe^{+++} + 7H_2O$.

Method A.—The valence of each chromium atom changes from +6 to +3, but the molecule of potassium dichromate

contains *two* chromium atoms. The total change in valence is therefore 6, and the equivalent weight of potassium dichromate is $\frac{K_2Cr_2O_7}{6} = 49.03$.

Method B.—A similar reaction with hydrogen gives:

$$K_2Cr_2O_7 + 6H + 4H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O.$$

$$\frac{K_2Cr_2O_7}{6} = 49.03.$$

Example III. Nitric Acid.—When nitric acid acts merely as a neutralizing agent, its equivalent weight and its molecular weight, 63.01, are identical as has been explained under acidimetry. When used as an oxidizing agent, however, the nitric acid is usually reduced to nitric oxide and the valence of the nitrogen changed from five to two:

$$3Cu + \underset{\text{(oxidizing)}}{2HNO_3} + 6HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O,$$

or $$3Cu^\circ + 2NO_3^- + 8H^+ \rightarrow 3Cu^{++} + 2NO + 4H_2O.$$

Method A.—Since the valence change of the nitrogen is from +5 to +2, the equivalent weight is $\frac{HNO_3}{3} = 21.00$.

Method B.—Since

$$HNO_3 + 3H \rightarrow NO + 2H_2O,$$

one hydrogen requires $\frac{HNO_3}{3} = 21.00$.

It is evident that a solution of nitric acid which is normal as an acid is 3 normal as an oxidizing agent.

When *concentrated* nitric acid acts as an oxidizing agent the nitrogen is usually reduced only to nitrogen peroxide (NO_2) representing a change in valence of the nitrogen from five to four. In this case the equivalent weight is $\frac{HNO_3}{1} = 63.01$.

Example IV. Iodine.—This substance dissolved in potassium iodide solution is used in volumetric analyses as an oxidizing agent. The iodine of the potassium iodide takes no active part in the oxidation process since it is already present in its lowest valence, but the dissolved iodine is reduced from a valence of zero to a valence of minus one; for example,

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI,$$

or $$2S_2O_3^= + I_2 \rightarrow S_4O_6^= + 2I^-$$

Method A.—Each atom of iodine changes in valence by one unit, but since there are two atoms to the molecule, the equivalent weight is $\frac{I_2}{2} = 126.92$.

Method B.—An equation with hydrogen gives:

$$I_2 + 2H \rightarrow 2HI,$$

and the iodine reacting with one hydrogen is $\frac{I_2}{2} = 126.92$. A normal solution of iodine therefore contains 126.92 grams of the pure solid in a liter of solution.

Example V. Iodate, Bromate, Chlorate.—These substances (in the form of water-soluble salts) are used in volumetric analyses as oxidizing agents, and the halogen is usually reduced from a valence of $+5$ to a valence of -1; for example,

$$KBrO_3 + 6KI + 3H_2SO_4 \rightarrow 3K_2SO_4 + KBr + 3I_2 + 3H_2O,$$

or $$BrO_3^- + 6I^- + 6H^+ \rightarrow Br^- + 3I_2 + 3H_2O.$$

Method A.—Since the change in valence of the bromine in this case is from $+5$ to -1, representing a change of six units, the equivalent weight of the potassium bromate is $\frac{KBrO_3}{6} = 27.84$.

Method B.—A hypothetical equation with hydrogen gives:

$$KBrO_3 + 6H \rightarrow KBr + 3H_2O,$$

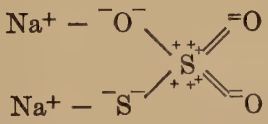
in which the equivalent weight is again $\frac{KBrO_3}{6} = 27.84$.

In the corresponding cases, the equivalent weights of KIO_3 and $KClO_3$ are $\frac{KIO_3}{6} = 35.67$, and $\frac{KClO_3}{6} = 20.43$ respectively. In some reactions, other reduction products of the oxy-halogen salts are obtained, and other equivalent weights must be taken. Thus, potassium chlorate is sometimes reduced in solution to chlorine dioxide (ClO_2) where the change in valence is from five to four and the equivalent weight of the potassium chlorate is $\frac{KClO_3}{1} = 122.56$.

Example VI. Sodium Thiosulphate.—This substance is used as a reducing agent usually in connection with titrations involving iodine. The reaction in this case is:

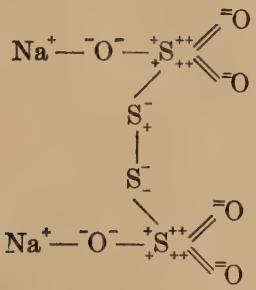
$$\underset{\text{(thiosulphate)}}{2Na_2S_2O_3} + I_2 \rightarrow \underset{\text{(tetrathionate)}}{Na_2S_4O_6} + 2NaI.$$

Method A.—Considering the valence change of the sulphur from a purely mathematical standpoint the valence is found to be +2 in the thiosulphate and +2½ in the tetrathionate, representing a change of one-half for each sulphur atom. Since the thiosulphate molecule contains two sulphur atoms, the valence of the molecule changes by one unit and the equivalent weight is $\frac{Na_2S_2O_3}{1} = 158.12$. Obviously an element cannot have a fractional valence, and the apparent contradiction to this lies in the fact that in the thiosulphate and tetrathionate molecules the valences of the sulphur atoms differ. Thus, the formula of sodium thiosulphate may be written in structural form as follows:



The valence of one sulphur atom is shown to be +6 and the valence of the other sulphur atom to be −2. The *average* valence is therefore +2.

The formula of sodium tetrathionate may be written graphically as follows:



Two sulphur atoms have a valence of +6, one has a valence of −2, and one has a valence of 0. The *average* valence is therefore +2½.

Method B.—A hypothetical equation with oxygen,

$$2Na_2S_2O_3 + O + H_2O \rightarrow Na_2S_4O_6 + 2NaOH,$$

shows that each molecule of sodium thiosulphate requires one-

half of an atom of oxygen, which in turn is equivalent to one atom of hydrogen. The equivalent weight of sodium thiosulphate is $\frac{Na_2S_2O_3}{1} = 158.12$.

Example VII. Oxalic Acid.—Oxalic acid is frequently used in analytical chemistry both as an acid and as a reducing agent. As an acid, two replaceable hydrogens are available and the equivalent weight is one-half of the molecular weight. As a reducing agent, oxalic acid is oxidized to carbon dioxide and water; for example,

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O,$$

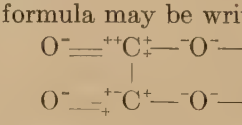
or

$$5C_2O_4^{=} + 2MnO_4^{-} + 16H^{+} \rightarrow 2Mn^{++} + 10CO_2 + 8H_2O.$$

Method A.—From a mathematical point of view, the valence of each carbon atom changes from +3 to +4, or a change of one. Since the molecule contains two carbon atoms, its equivalent weight as a reducing agent is $\frac{H_2C_2O_4}{2} = 45.01$, or $\frac{H_2C_2O_4.2H_2O}{2} = 63.02$, depending on the form of oxalic acid referred to. As in the case of sodium thiosulphate above, the two atoms in the molecule actually have different valences, for on dehydration, oxalic acid breaks down into carbon monoxide and carbon dioxide:

$$H_2C_2O_4 \rightarrow H_2O + CO + CO_2$$

and the structural formula may be written:



Method B.—The same oxidation may be written hypothetically:

$$H_2C_2O_4 + O \rightarrow 2CO_2 + H_2O,$$

where the equivalent weight of oxalic acid is likewise $\frac{H_2C_2O_4}{2} = 45.01$, or $\frac{H_2C_2O_4.2H_2O}{2} = 63.02$.

Example VIII. Acid Oxalates.—The equivalent weight of potassium acid oxalate, KHC_2O_4, as an acid is obviously $\frac{KHC_2O_4}{1}$

= 128.12, there being one replaceable hydrogen. As a reducing agent, the same considerations hold as in the case of oxalic acid above, and the equivalent weight is $\frac{KHC_2O_4}{2} = 64.06$. This weight in grams in a liter of solution constitutes a normal solution as a reducing agent, but the same solution is only half normal as an acid. Conversely, a solution of potassium hydrogen oxalate which is normal as an acid contains 128.12 grams of the salt per liter and is two normal as a reducing agent.

Another oxalate which is used in volumetric work is potassium tetroxalate, $KHC_2O_4.H_2C_2O_4.2H_2O$. This salt has three replaceable hydrogens and two oxalate radicals, and for purposes of calculation may be considered as $KHC_2O_4 + H_2C_2O_4.2H_2O$. Hence, from the above considerations, it is apparent that as an acid, the equivalent weight, of potassium tetroxalate is one-third of its molecular weight, or 84.72, and as a reducing agent, the equivalent weight is one-fourth of the molecular weight, or 63.54. A solution of potassium tetroxalate which is normal as an acid is therefore four-thirds normal as a reducing agent; and a solution of potassium tetroxalate which is normal as a reducing agent is three-fourths normal as an acid.

EXAMPLE IX. PEROXIDES.—Hydrogen peroxide (H_2O_2) can act both as an oxidizing agent and as a reducing agent. As an oxidizing agent, one oxygen (equivalent to two hydrogens) from each molecule is available for oxidation:

$$H_2O_2 \rightarrow H_2O + O,$$

and water is left as the reduction product; for example,

$$2FeSO_4 + H_2O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2H_2O.$$

Obviously, therefore, the equivalent weight of hydrogen peroxide as an oxidizing agent is $\frac{H_2O_2}{2} = 17.008$.

As a reducing agent, one oxygen (equivalent to two hydrogens) from each molecule is capable of uniting with an oxygen atom from the substance reduced, to form oxygen gas. Thus,

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \rightarrow K_2SO_4 + 2\,MnSO_4 + 8H_2O + 5O_2,$$

or in general,

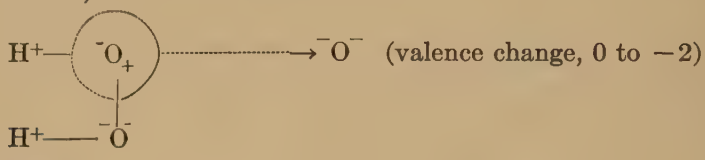
$$H_2O_2 + O \text{ (from oxidizing agent)} \rightarrow H_2O + O_2.$$

Hence, as a reducing agent hydrogen peroxide likewise has an equivalent weight of $\frac{H_2O_2}{2} = 17.008$.

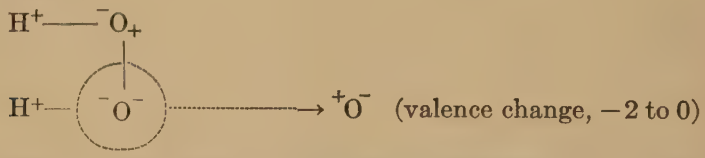
The structural formula of hydrogen peroxide is usually written with the electrical charges distributed as follows:

$$H^+—{}^-O_+$$
$$\quad\quad|$$
$$H^+—{}^-O^-.$$

On reduction,



On oxidation,



EXAMPLE X. SULPHUR.—In analytical chemistry, the element sulphur is usually encountered in the following forms:

CONDITION	VALENCE
H_2S, sulphides	−2
S (free)	0
SO_2, H_2SO_3, sulphites	+4
SO_3, H_2SO_4, sulphates	+6

Since all these forms may be converted more or less readily one into another, it follows that there a large number of possible valence changes, and that sulphur may have one of several equivalent weights, depending upon the reaction involved. In the reaction:

$$3H_2S + 2HNO_3 \rightarrow 3S + 2NO + 4H_2O,$$

the valence change of the sulphur is from −2 to 0 and the equivalent weight of H_2S is $\frac{H_2S}{2} = 17.04$, and that of the constituent sulphur is $\frac{S}{2} = 16.03$. In the oxidation of sulphurous acid, as for example in the reaction:

$$H_2SO_3 + H_2O + I_2 \rightarrow H_2SO_4 + 2HI,$$

the valence change of the sulphur is from +4 to +6 and the equivalent weights are therefore $\frac{H_2SO_3}{2} = 41.04$, $\frac{SO_2}{2} = 32.03$, and $\frac{S}{2} = 16.03$ as the case may be. In the determination of sulphur in steel by the Bamber method, the sulphur, probably present as manganese sulphide, is oxidized directly by strong nitric acid according to the reaction:

$$MnS + 8HNO_3 \rightarrow MnSO_4 + 8NO_2 + 4H_2O.$$

Here the valence of the sulphur undergoes a change from −2 to +6 and the equivalent weight of the sulphur is $\frac{S}{8} = 4.008$. Other changes are possible, and each change will give a characteristic equivalent weight for the reacting sulphur.

Consideration of the above, especially Examples I, III, V, VII, VIII, IX, and X, shows the importance of the following fact which cannot be over emphasized, namely, *the equivalent weight of an element or compound depends entirely upon the reaction in which that element or compound is involved.*

54. Calculations of Oxidation and Reduction Processes.— Since the concentration of solutions in oxidation and reduction titrations, like those in acidimetry and alkalimetry, are based on the hydrogen equivalent, the methods of calculation are identical. Thus, 1 liter of a normal solution of an oxidizing agent will exactly oxidize 1 liter of a normal solution of a reducing agent, or 2 liters of a half normal solution.

$$V_1N_1 = V_2N_2 \text{ (cf. Sec. 41)}$$

In titrating a reducing agent with a solution of oxidizing agent, or an oxidizing agent with a solution of reducing agent, reasoning similar to that described in Secs. 42 and 43 will evolve the same general formulae as were there derived, namely,

$$c.c._s \times N_s \times e_x = grams_x$$

and

$$\frac{c.c._s \times N_s \times e_x}{weight\ of\ sample} \times 100 = per\ cent_x.$$

The methods of solving the various types of problems described under Secs. 43, 44, and 45 likewise apply to oxidation and reduction titrations.

Permanganate Process

EXAMPLE I.—What is the normality of a solution of potassium permanganate if 40.00 c.c. will oxidize that weight of potassium tetroxalate, $KHC_2O_4.H_2C_2O_4.2H_2O$, which requires 30.00 c.c. of N/2 sodium hydroxide solution for its neutralization?

The amount of tetroxalate which requires 30.00 c.c. of N/2 NaOH for neutralization is:

$$30.00 \times 0.5000 \times \frac{KHC_2O_4.H_2C_2O_4.2H_2O}{3{,}000} = 1.271 \text{ grams.}$$

The normality of the permanganate is therefore:

$$\frac{1.271}{40.00 \times \frac{KHC_2O_4.H_2C_2O_4.2H_2O}{4{,}000}} = 0.5000. \quad \textit{Ans.}$$

The same result is more simply obtained by setting up the entire equation before performing any of the operations, when it will be found that the molecular weights of the potassium tetroxalate cancel and need not be calculated. Thus, the weight of potassium tetroxalate neutralized by 30.00 c.c. of N/2 NaOH is

$$30.00 \times 0.5000 \times \frac{KHC_2O_4.H_2C_2O_4.2H_2O}{3{,}000},$$

and the weight of potassium tetroxalate oxidized by 40.00 c.c. of x normal $KMnO_4$ is

$$40.00 \times x \times \frac{KHC_2O_4.H_2C_2O_4.2H_2O}{4{,}000}.$$

Since these two expressions are equal to each other, the equality may be expressed by an equation in which the molecular weights of the potassium tetroxalate cancel, and x gives the value 0.5000 for the normality of the permanganate.

EXAMPLE II.—What is the percentage of iron in a sample of iron ore weighing 0.7100 gram if after solution and reduction of the iron with amalgamated zinc, 48.06 c.c. of $KMnO_4$ (1 c.c. $=$ 0.006700 gram $Na_2C_2O_4$) are required to oxidize the iron? How many grams of $KMnO_4$ are contained in each cubic centimeter of the solution?

$$\text{Normality of the } KMnO_4 = \frac{0.006700}{\frac{Na_2C_2O_4}{2{,}000}} = 0.1000 \text{ N}$$

$$\frac{48.06 \times 0.1000 \times \frac{Fe}{1{,}000}}{0.7100} \times 100 = 37.80 \text{ per cent Fe.} \quad \textit{Ans.}$$

Each cubic centimeter of normal $KMnO_4$ contains $\frac{KMnO_4}{5{,}000} = 0.03161$ gram.

Each cubic centimeter of this $KMnO_4$ contains $0.03161 \times 0.1000 = 0.003161$ gram. *Ans.*

EXAMPLE III.—How many grams of H_2O_2 are contained in a solution which requires for titration 14.05 c.c. of $KMnO_4$ of which 1 c.c. $\doteq$ 0.008376 gram Fe (*i.e.*, will oxidize that amount of iron from the divalent to the trivalent state)? How many grams and how many cubic centimeters of oxygen measured dry and under standard conditions are evolved during the titration?

$$\text{Normality } KMnO_4 = \frac{0.008376}{\frac{Fe}{1{,}000}} = 0.1500 \text{ N.}$$

$$\text{Grams } H_2O_2 = 14.05 \times 0.1500 \times \frac{H_2O_2}{2{,}000} = 0.03584 \text{ gram.} \quad \textit{Ans.}$$

Each mole of H_2O_2 corresponds to a mole of O_2 evolved (see equation above).

$$\text{Therefore grams } O_2 \text{ evolved} = 14.05 \times 0.1500 \times \frac{O_2}{2{,}000}$$
$$= 0.03372 \text{ gram.} \quad \textit{Ans.}$$

Each gram-mole of O_2 occupies 22,400 c.c.

$$\text{Therefore cubic centimeters of } O_2 \text{ evolved} = 14.05 \times 0.1500 \times \frac{22{,}400}{2{,}000} = 23.60 \text{ c.c.} \quad \textit{Ans.}$$

EXAMPLE IV.—What is the percentage of MnO_2 in impure pyrolusite if a sample weighing 0.4000 gram is treated with 0.6000 gram of pure $H_2C_2O_4.2H_2O$ and dilute H_2SO_4 and after reduction has taken place ($MnO_2 + H_2C_2O_4 + 2H^+ \rightarrow Mn^{++} + 2CO_2 + 2H_2O$) the excess oxalic acid requires 26.26 c.c. of N/10 $KMnO_4$ for titration?

Volume of $KMnO_4$ equivalent to the total $H_2C_2O_4.2H_2O$ added =

$$\frac{0.6000}{0.1 \times \frac{H_2C_2O_4.2H_2O}{2{,}000}} = 95.26 \text{ c.c.}$$

Net volume $KMnO_4$ (equivalent to MnO_2 in the sample) = 95.26 − 26.26 = 69.00 c.c.

$$\frac{69.00 \times 0.1 \times \frac{MnO_2}{2{,}000}}{0.4000} \times 100 = 74.97 \text{ per cent } MnO_2. \quad \textit{Ans.}$$

EXAMPLE V.—A steel containing 0.90 per cent Mn is analyzed by the three standard methods below, in each case using a 2.50-gram sample, N/12 $KMnO_4$ and N/10 $FeSO_4$ solutions. Calculate in each case the volume of $KMnO_4$ required.

Bismuthate or *Persulphate Method.*—The Mn is oxidized to $KMnO_4$ and after reducing with 25 c.c. of standard $FeSO_4$ ($MnO_4^- + 5Fe^{++} + 8H^+ \rightarrow Mn^{++} + 5Fe^{+++} + 4H_2O$) the excess ferrous iron is titrated with the standard $KMnO_4$.

Let x = cubic centimeters of $KMnO_4$ used in the titration.

$$25 \text{ c.c. } FeSO_4 \simeq 25 \times \frac{12}{10} = 30 \text{ c.c. } KMnO_4.$$

Net cubic centimeters of $KMnO_4$ (equivalent to Mn in the steel) = $30 - x$.

$$\frac{(30 - x)\frac{1}{12} \times \frac{Mn}{5{,}000}}{2.50} \times 100 = 0.90$$

$$x = 5.42 \text{ c.c.} \quad \textit{Ans.}$$

Williams Method.—The Mn is oxidized to MnO_2 which is filtered and dissolved in 25 c.c. of the standard $FeSO_4$ ($MnO_2 + Fe^{++} + 4H^+ \rightarrow Mn^{++} + 2Fe^{+++} + 2H_2O$). The excess $FeSO_4$ is titrated with the standard $KMnO_4$.

Let x = cubic centimeters of $KMnO_4$ used in the titration.

$$25 \text{ c.c. } FeSO_4 \simeq 25 \times \frac{12}{10} = 30 \text{ c.c. } KMnO_4.$$

Net cubic centimeters of $KMnO_4$ (equivalent to Mn in the steel) = $30 - x$.

$$\frac{(30 - x)\frac{1}{12} \times \frac{Mn}{2{,}000}}{2.50} \times 100 = 0.90$$

$$x = 20.17 \text{ c.c.} \quad \textit{Ans.}$$

Volhard Method.—The Mn is directly titrated in neutral solution with standard $KMnO_4$ ($3Mn^{++} + 3MnO_4^- + 2H_2O \rightarrow 5MnO_2 + 4H^+$).

Let x = cubic centimeter of $KMnO_4$ used in the titration.

In this case the normality of the $KMnO_4$ cannot be taken as N/12 because it is used in neutral solution where its valence change is 3 instead of 5 (see Sec. 53, Example I). In other words the oxidizing power of $KMnO_4$ in neutral solution is only three-fifths as great as it is in acid solution. In this particular case the normality is $\frac{1}{12} \times \frac{3}{5}$. The valence change of the titrated Mn is 2.

$$\frac{x\left(\frac{1}{12} \times \frac{3}{5}\right)\frac{\text{Mn}}{2{,}000}}{2.50} \times 100 = 0.90$$

$$x = 16.38 \text{ c.c.} \quad \textit{Ans.}$$

Dichromate Process

EXAMPLE VI.—What is the percentage of Fe_2O_3 in a sample of limonite ore (impure Fe_2O_3) if the iron from a 0.5000-gram sample is reduced and titrated with 35.15 c.c. of a potassium dichromate solution of which 15.00 c.c. are equivalent in oxidizing power to 25.00 c.c. of a potassium permanganate solution of which 1 c.c. $\simeq$ 0.004750 gram Fe. (This last expression is a conventional means of signifying that 1 c.c. of the solution will oxidize 0.004750 gram of iron *from the divalent to the trivalent state.*)

$$\text{Normality of the } KMnO_4 = \frac{0.004750}{1 \times \frac{\text{Fe}}{1{,}000}} = 0.08506.$$

$$\text{Normality of } K_2Cr_2O_7 = 0.08506 \times \frac{25.00}{15.00} = 0.1418$$

$$\frac{35.15 \times 0.1418 \times \frac{Fe_2O_3}{2{,}000}}{0.5000} \times 100 = 79.56 \text{ per cent } Fe_2O_3. \quad \textit{Ans.}$$

EXAMPLE VII.—Fusion with Na_2O_2 oxidizes the chromium in a 0.2000-gram sample of chromite ore to chromate. The addition of a 50-c.c. pipetteful of ferrous sulphate solution reduces this in acid solution to chromic salt ($Cr_2O_7^- + 6Fe^{++} + 14H^+ \rightarrow 2Cr^{+++} + 6Fe^{+++} + 7H_2O$) and the excess ferrous ions are titrated with 7.59 c.c. of N/10 $K_2Cr_2O_7$. Each pipetteful of

ferrous solution is equivalent to 47.09 c.c. of the standard $K_2Cr_2O_7$ solution. What is the percentage of Cr in the sample? What weight of sample of the chromite ore should be taken such that the cubic centimeters of standard N/10 $K_2Cr_2O_7$ which are equivalent to the ferrous solution added, minus the cubic centimeter of K_2CrO_7 used in the titration will equal the per cent of Cr_2O_3 in the sample?

Net $K_2Cr_2O_7$ solution (equivalent to the Cr in the ore) = 47.09 − 7.59 = 39.50 c.c.

$$\frac{39.50 \times 0.1000 \times \frac{Cr}{3{,}000}}{0.2000} \times 100 = 34.23 \text{ per cent Cr.} \quad \textit{Ans.}$$

The second part of this problem merely states that the net volume of N/10 $K_2Cr_2O_7$ (*i.e.*, the c.c. equivalent to the Cr in the sample) is equal in value to the per cent Cr_2O_3.

$$\frac{a \times 0.1000 \times \frac{Cr_2O_3}{6{,}000}}{x} \times 100 = a$$

$$x = 0.2533 \text{ gram.} \quad \textit{Ans.}$$

Iodimetric Process

Example VIII.—An excess of potassium iodide is added to a solution of potassium dichromate, and the liberated iodine is titrated with 48.80 c.c. of N/10 sodium thiosulphate solution. How many grams of $K_2Cr_2O_7$ did the dichromate solution contain?

This determination makes use of the fact that a strong oxidizing agent like potassium dichromate will liberate *its own equivalent* of iodine from an iodide:

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 \rightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O,$$

and the liberated iodine may be titrated with thiosulphate:

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI.$$

Although the titrating agent does not react directly with the dichromate, it reacts with its equivalent of iodine. Therefore, the volume of titrating solution is the same as it would have been if the original solution had been titrated directly. This is true of all similar determinations.

Hence,

$$\text{Grams of } K_2Cr_2O_7 = 48.80 \times 0.1000 \times \frac{K_2Cr_2O_7}{6{,}000} = 0.2393. \textit{ Ans.}$$

EXAMPLE IX.—The sulphur from 4.0 grams of steel is evolved as H_2S and titrated with 1.60 c.c. of N/20 iodine solution. What is the percentage of S in the steel? What is the value of 1 c.c. of the iodine in terms of As_2O_3? How many cubic centimeters of the iodine will be reduced by 40 c.c. of $Na_2S_2O_3$ solution of which 1 c.c. = 0.006357 gram Cu. The equations involved are as follows:

$$H_2S + I_2 \rightarrow S + 2HI$$

$$Na_3AsO_3 + 2NaHCO_3 + I_2 \rightarrow Na_3AsO_4 + NaI + 2CO_2 + H_2O$$

$$2Cu^{++} + 4I^- \rightarrow Cu_2I_2 + I_2$$

$$\frac{1.60 \times \frac{1}{20} \times \frac{S}{2{,}000}}{4.0} \times 100 = 0.032 \text{ per cent S.} \quad \textit{Ans.}$$

$$1 \times \frac{1}{20} \times \frac{As_2O_3}{4{,}000} = 0.002474 \text{ gram } As_2O_3. \quad \textit{Ans.}$$

The addition of KI to a copper solution will cause reduction of the Cu and the liberation of an amount of iodine equivalent to the copper present. This iodine may be titrated with thiosulphate and the normality of the latter found from the amount of Cu present. In the above case,

$$\text{Normality of } Na_2S_2O_3 \text{ solution} = \frac{0.006357}{1 \times \frac{Cu}{1{,}000}} = 0.1000 \text{ N}$$

$$\text{Volume of N/20 } I_2 \text{ solution} = 40 \times \frac{0.10}{0.05} = 80 \text{ c.c.} \quad \textit{Ans.}$$

Problems

236. How many grams of KNO_2 per cubic centimeter does a solution of potassium nitrite contain if it is tenth normal as a reducing agent? How many grams of SO_2 per liter does a sulphurous acid solution contain which is 0.05860 N as a reducing agent?

Ans. 0.004256 gram.
1.876 grams.

237. Calculate the value of 1 c.c. of 0.1242 N $KMnO_4$ in terms of (*a*) Fe; (*b*) Fe_2O_3; (*c*) $FeSO_4.7H_2O$. Calculate the value of 1 c.c. of 0.1242 N iodine solution as an oxidizing agent in terms of (*a*) SO_2; (*b*) H_2SO_3; (*c*) Na_2SO_3.

Ans. (*a*) 0.006934 gram; (*b*) 0.009917 gram; (*c*) 0.03451 gram.
(*a*) 0.003978 gram; (*b*) 0.005097 gram; (*c*) 0.007829 gram.

238. What is the normality of a nitric acid solution to be used as an oxidizing agent (reduced to NO) if it contains 55.5 per cent by weight of HNO_3 and has a specific gravity of 1.350?

Ans. 35.67 N.

239. Thirty cubic centimeters of ferrous ammonium sulphate solution contain 1.176 grams of pure $FeSO_4.(NH_4)_2SO_4.6H_2O$. Twenty cubic centimeters of potassium dichromate solution contain 0.2940 gram of $K_2Cr_2O_7$. Calculate (*a*) Normality of the ferrous ammonium sulphate? (*b*) Normality of the dichromate? (*c*) Value of 1 c.c. of ferrous solution in terms of the dichromate solution?

Ans. (*a*) 0.1000 N; (*b*) 0.2998 N; (*c*) 0.3335 c.c.

240. What is the value of 1 c.c. of N/25 sodium thiosulphate solution in terms of Cu? $(2Cu^{++} + 4I^- \rightarrow 2CuI + I_2)$. What is the normality of a thiosulphate solution if 25 c.c. are required to titrate the iodine liberated by 0.01563 gram of copper?

Ans. 0.002543 gram.
0.009833 N.

241. How many cubic centimeters of $K_2Cr_2O_7$ solution containing 25.00 grams of anhydrous salt per liter would react with 3.400 grams of $FeSO_4.7H_2O$ in dilute acid solution?

Ans. 24.00 c.c.

242. An iodine solution which has been standardized and found to be 1.003 normal is 0.3 per cent too strong. How many cubic centimeters of N/100 iodine must be added to a liter of the first solution to make it of the desired strength?

Ans. 3.03 c.c.

243. If 10 grams of $K_4Fe(CN)_6.3H_2O$ are dissolved in water and the volume made up to 500 c.c., what is the normality of the solution as a reducing agent? $(10K_4Fe(CN)_6 + 2KMnO_4 + 8H_2SO_4 \rightarrow 10K_3Fe(CN)_6 + 6K_2SO_4 + 2MnSO_4 + 8H_2O)$.

Ans. 0.04736 N.

244. One cubic centimeter $KHC_2O_4.H_2C_2O_4.2H_2O \simeq 0.2000$ c.c. $KMnO_4$.
One cubic centimeter $KMnO_4 \simeq 0.1117$ gram Fe.
What is the normality of the tetroxalate solution when used as a reducing agent?

Ans. 0.4000 N.

245. What is the value of 1 c.c. of an iodine solution (1 c.c. $\simeq$ 0.03000 gram $Na_2S_2O_3$) in terms of As_2O_3? $(Na_3AsO_3 + I_2 + 2NaHCO_3 \rightarrow Na_3AsO_4 + 2NaI + H_2O + 2CO_2)$.

Ans. 0.009386 gram.

246. Calcium may be precipitated as $CaC_2O_4.H_2O$, the precipitate filtered, washed, and dissolved in dilute H_2SO_4. The oxalic acid formed may be titrated with potassium permanganate. If a N/10 solution of $KMnO_4$ is used, calculate the value of 1 c.c. in terms of (*a*) Ca; (*b*) CaO; (*c*) $CaCO_3$.

Ans. (*a*) 0.002004 gram.
(*b*) 0.002804 gram.
(*c*) 0.005004 gram.

247. One hundred cubic centimeters of $K_2Cr_2O_7$ solution (10.0 grams per liter), 5.00 c.c. of 6 N H_2SO_4 and 75.0 c.c. of $FeSO_4$ solution (80.0 grams $FeSO_4.7H_2O$ per liter) are mixed and the resulting solution titrated with 0.2121 N $KMnO_4$. Calculate the volume required.

Ans. 5.63 c.c.

248. To a mixture of 97.31 c.c. of 0.1096 normal iodine and 97.21 c.c. of 0.1098 normal thiosulphate solution a drop of starch is added. Is the solution blue or colorless?

Ans. Colorless.

249. One-tenth of a gram of iron (99.98 per cent pure) was dissolved in sulphuric acid out of contact with the air and was titrated with 0.1 N $KMnO_4$. How many cubic centimeters were used in the titration?

Ans. 17.91 c.c.

250. From the following data calculate the normality of the $Na_2S_2O_3$ solution.

1 c.c. $K_2Cr_2O_7 \simeq 0.005584$ gram of Fe.

20 c.c. $K_2Cr_2O_7$ liberates sufficient iodine from potassium iodide to require 32.46 c.c. $Na_2S_2O_3$ solution for reduction.

Ans. 0.06162 N.

251. Fifty cubic centimeters of an iodine solution are exactly equivalent in oxidizing power to 49.47 c.c. of a $K_2Cr_2O_7$ solution of which 1 c.c. will liberate 0.004263 gram of iodine from KI. Calculate the normal values.

Ans. I_2 = 0.03323 N.
$K_2Cr_2O_7$ = 0.03359 N.

252. From the following data calculate the ratio of the nitric acid as an oxidizing agent to the tetroxalate solution as a reducing agent.

1 c.c. $HNO_3 \simeq 1.246$ c.c. NaOH
1 c.c. $KHC_2O_4.H_2C_2O_4.2H_2O \simeq 1.743$ c.c. NaOH
Normality NaOH = 0.1200

Ans. 1.608.

253. Forty cubic centimeters of $KMnO_4$ solution (1 c.c. $\simeq$ 0.005000 gram iron) are added to KI and the liberated iodine titrated with sodium thiosulphate solution requiring 35.90 c.c. What is the value of 1 c.c. of the thiosulphate solution in terms of copper? ($2Cu^{++} + 4I^- \rightarrow 2CuI + I_2$.)

Ans. 0.006345 gram.

254. What weight of $FeSO_4.7H_2O$ will react with that amount of MnO_2 (92.50 per cent pure) which will oxidize the same amount of oxalic acid as 35 c.c. of $KMnO_4$ solution of which 1 c.c. will liberate 0.01750 gram of iodine from KI. ($MnO_2 + 2Fe^{++} + 4H^+ \rightarrow Mn^{++} + 2Fe^{+++} + 2H_2O$.)

Ans. 1.342 grams.

255. Given two permanganate solutions. Solution A contains 0.01507 gram of $KMnO_4$ per cubic centimeter. Solution B is of such strength that 20 c.c. = 0.1200 gram Fe. In what proportion must the two solutions be mixed in order that the resulting solution shall have the same oxidizing power in the presence of acid as N/3 $K_2Cr_2O_7$ has?

Ans. $\frac{\text{Vol. A}}{\text{Vol. B}} = 1.576$

256. If 25 c.c. of ferrous sulphate solution in sulphuric acid require 31.25 c.c. of N/10 $K_2Cr_2O_7$ solution for oxidation, how much water must be added to 200 c.c. of the reducing solution to make it exactly one-twentieth normal?

Ans. 300 c.c.

257. To oxidize the iron in 1 gram of $FeSO_4.(NH_4)_2SO_4.6H_2O$ requires 5 c.c. of HNO_3. How much water must be added to 500 c.c. of this acid to make the concentration as an acid exactly one-tenth normal?

Ans. 350 c.c.

258. A solution of sodium thiosulphate is freshly prepared and 48 c.c. are required to titrate the iodine liberated from an excess of KI solution by 0.3000 gram of pure KIO_3. ($KIO_3 + 5KI + 3H_2SO_4 \rightarrow 3K_2SO_4 + 3I_2 + 3H_2O$). What is the normality of the thiosulphate and its value in terms of iodine?

Ans. 0.1752 N.
0.02224 gram.

259. The thiosulphate solution of the preceding problem is allowed to stand and 1 per cent of the $Na_2S_2O_3$ is decomposed by carbonic acid present in the solution ($Na_2S_2O_3 + 2H_2CO_3 \rightarrow H_2SO_3 + 2NaHCO_3 + S$). What is the new normality of the solution as a reducing agent?

Ans. 0.1768 N. (Note the *increase* in strength.)

260. How many grams of $KMnO_4$ are contained in a liter of potassium permanganate if a certain volume of it will oxidize a weight of potassium tetroxalate requiring one-half that volume of N/5 potassium hydroxide solution for neutralization?

Ans. 4.214 grams.

261. What is the normality of a solution of potassium permanganate if 50.13 c.c. will oxidize that weight of KHC_2O_4 which requires 43.42 c.c. of 0.3010 N sodium hydroxide for neutralization?

Ans. 0.5214 N.

262. If the iron in a 0.1500-gram sample of iron ore is reduced and subsequently requires 15.03 c.c. of N/10 permanganate for oxidation, what is the purity of the ore expressed as percentage of (*a*) Fe; (*b*) FeO; (*c*) Fe_2O_3?

Ans. (*a*) 55.94 per cent.
(*b*) 71.96 per cent.
(*c*) 79.98 per cent.

263. What is the percentage purity of a sample of impure $H_2C_2O_4.2H_2O$ if a sample weighing 0.2003 gram requires 29.30 c.c. of permanganate solution, of which 1 c.c. $\simeq$ 0.006023 gram Fe?

Ans. 99.53 per cent.

264. A sample of sodium sulphite weighing 1.468 grams was added to 100 c.c. of N/10 iodine. The excess iodine was titrated with 42.40 c.c. of $Na_2S_2O_3.5H_2O$ solution of which 1 c.c. was equivalent to the iodine liberated from 0.01574 gram of KI. Calculate the percentage of Na_2SO_3 in the sample.

Ans. 25.67 per cent.

265. Given the following data, calculate the percentage of MnO_2 in a sample of pyrolusite.

Sample = 0.5217 gram.

$KHC_2O_4.H_2C_2O_4.2H_2O$ added to react with MnO_2 = 0.7242 gram.

$KMnO_4$ used in titrating excess = 22.42 c.c.

1 c.c. $KMnO_4 \simeq$ 0.009721 gram $H_2C_2O_4.2H_2O$.

($MnO_2 + C_2O_4^{=} + 4H^+ \rightarrow Mn^{++} + 2CO_2 + 2H_2O$.)

Ans. 66.14 per cent.

266. From the following data calculate the chromium content in terms of the percentage of Cr and of Cr_2O_3 in a sample of chrome iron ore: Weight of sample = 0.2500 gram; $FeSO_4$ solution used = 53.40 c.c.; $K_2Cr_2O_7$ solution used = 8.00 c.c.; 1 c.c. $FeSO_4$ solution $\simeq$ 0.8000 c.c. $K_2Cr_2O_7$ solution; 20.00 c.c. $K_2Cr_2O_7$ solution liberates from an excess of KI an amount of iodine requiring 25.00 c.c. of N/10 $Na_2S_2O_3$ for reduction. ($Cr_2O_7^{=} + 6Fe^{++} + 14H^+ \rightarrow Cr^{+++} + 6Fe^{+++} + 7H_2O$.)

Ans. Cr = 30.08 per cent.
Cr_2O_3 = 43.97 per cent.

267. If an element has 98 for its atomic weight, and after reduction with stannous chloride, could be oxidized by dichromate to the form corresponding to an $XO_4^{=}$ anion, compute the oxide corresponding to the reduced state from the following data: 0.3266 gram of the pure element after being dissolved was reduced with $SnCl_2$ and oxidized by 40.00 c.c. of $K_2Cr_2O_7$ solution, of which 1 c.c. $\simeq$ 0.1960 gram of $FeSO_4.(NH_4)_2SO_4.6H_2O$.

Ans. X_2O.

268. A sample of stibnite containing 70.00 per cent Sb is given to a student for analysis. He titrates with a solution of iodine of which he had found 1 c.c. to be equivalent to 0.004948 gram of As_2O_3. The normality of the solution, however, had changed, due to volatilization of iodine, and the student reports 70.25 per cent Sb. What is the percentage error, the present normality of the iodine solution, and how much N/5 iodine solution must be added to 1 liter of the solution to bring it back to its original strength? ($Na_3SbO_3 + I_2 + 2NaHCO_3 \rightarrow Na_3SbO_4 + 2NaI + 2CO_2 + H_2O$).

Ans. 0.36 per cent.
0.09965 N.
3.5 c.c.

269. A mixture of pure potassium permanganate and pure potassium chromate weighing 0.2400 gram, when treated with KI in acid solution, liberates sufficient iodine to react with 60.00 c.c. of N/10 sodium thiosulphate solution. Find the percentages of Cr and Mn in the mixture.

Ans. Cr = 11.0 per cent.
Mn = 20.5 per cent.

270. To a half-gram sample of pyrolusite is added a certain weight of oxalic acid ($H_2C_2O_4.2H_2O$) and after reaction in acid solution is complete, the excess oxalic acid requires 30.00 c.c. of N/10 $KMnO_4$ for oxidation. If the pyrolusite is calculated to contain 86.93 per cent MnO_2, what is the weight of oxalic acid added? ($MnO_2 + H_2C_2O_4 + H_2SO_4 \rightarrow MnSO_4 + 2CO_2 + 2H_2O$.)

Ans. 0.8194 gram.

271. Fifty cubic centimeters of 0.2016 N oxalic acid are added to a sample of pure MnO_2 to reduce it. The excess of oxalic acid requires 10.15 c.c. of 0.2008 N $KMnO_4$ for its oxidation. What weight of MnO_2 is present?

Ans. 0.3490 gram.

272. A sample of pyrolusite is treated with HCl, the liberated chlorine is passed into potassium iodide, and the liberated iodine is titrated with $Na_2S_2O_3$ solution (49.64 grams of $Na_2S_2O_3.5H_2O$ per liter). If 38.70 c.c. are required, what volume of N/4 $KMnO_4$ would be required in an indirect determination in which a similar sample is reduced with 0.9000 gram of $H_2C_2O_4.2H_2O$ and the excess oxalic acid is titrated with the $KMnO_4$?

$$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2,$$
$$Cl_2 + 2KI \rightarrow 2KCl + I_2.$$

Ans. 26.16 c.c.

273. A sample of pyrolusite weighing a grams is analyzed as in Problem 270. If the oxalic acid taken weighs b grams and c c.c. of N/10 $KMnO_4$ are used in the analysis, derive an expression showing the per cent MnO_2 in the sample.

Ans. $\dfrac{68.98b - 0.4347c}{a}$ = per cent.

274. In analyzing a 1-gram sample of hydrogen peroxide with permanganate, what must be the normality of the $KMnO_4$ in order that the burette reading shall represent directly the per cent H_2O_2?

Ans. 0.5880 N.

275. What weight of spathic iron ore (impure $FeCO_3$) should be taken for analysis such that the number of cubic centimeters of $KMnO_4$ (1 c.c. $\simeq$ 0.30 c.c. of potassium tetroxalate solution which is one-fourth normal as an acid) used in the titration will be twice the percentage of FeO in the ore?

Ans. 1.438 grams.

276. What must be the normality of a standard iodine solution so that if a 0.5000-gram sample of stibnite (impure Sb_2S_3) is taken for analysis, the

number of cubic centimeters of solution may represent directly the percentage of antimony? ($SbO_3^{=} + I_2 + H_2O \rightarrow SbO_4^{=} + 2H^+ + 2I^-$.)

Ans. 0.08212 N.

277. A sample of spathic iron ore is analyzed for calcium by the permanganate method, following the precipitation of the calcium as oxalate. What weight of sample must be taken so that one-half the number of cubic centimeters of N/10 $KMnO_4$ may represent the percentage of CaO in the sample?

Ans. 0.5607 gram.

278. How many grams of pure $K_2Cr_2O_7$ must be weighed out, dissolved, and diluted to exactly 700 c.c. to make a solution which when used in the titration of iron in a sample of ore shall be of such a strength that four times the number of cubic centimeters used with a half-gram sample shall represent one-half the percentage of FeO in the sample.

Ans. 19.12 grams.

279. What weight of iron ore should be taken for analysis so that the cubic centimeters of twelfth normal permanganate multiplied by two will give the per cent Fe_2O_3 in the sample?

Ans. 0.3328 gram.

280. In determining titanium volumetrically by means of ferric alum solution, what weight of sample should be taken so that the number of cubic centimeters of ferric alum solution (of which 50.00 c.c. yields 0.4000 gram of Fe_2O_3) shall be in the ratio to the percentage of Ti in the sample as 13 is to 4? ($Ti^{+++} + Fe^{+++} \rightarrow Ti^{++++} + Fe^{++}$.)

Ans. 1.566 grams.

281. If 0.9000 gram of oxalic acid ($H_2C_2O_4.2H_2O$) is allowed to react with 0.5000 gram of pyrolusite and the excess oxalic acid is titrated with permanganate, what must be the normality of the permanganate in order that one-half the percentage of MnO_2 may be obtained by subtracting the burette reading from a certain number? What is that number?

Ans. 0.2300 N; 62.09.

282. What weight of chromite should be taken for analysis so that by using 100 c.c. of 0.1250 normal ferrous sulphate solution to reduce the chromium after oxidation to dichromate and titrating the excess of the ferrous sulphate with 0.1111 normal dichromate solution, the percentage of Cr_2O_3 present can be found as follows:

112.5 − cubic centimeters of $K_2Cr_2O_7$ = per cent Cr_2O_3.

Ans. 0.2814 gram.

CHAPTER XI

SATURATION OR PRECIPITATION METHODS

55. Calculations Involved.—The methods of analysis classified under this subdivision depend upon the exact precipitation of a substance by a standard solution of a precipitating agent. The methods may be direct or indirect; that is, the precipitating agent may be added to a direct end point, or an excess may be added and that excess determined by titration. The methods of computation and the principles involved are exactly similar to those discussed under acidimetry and alkalimetry. In this case, however, elements and radicals other than hydrogen enter into the metatheses, and to determine the equivalent weight it is only necessary to divide the molecular weight by the actual valence or total electrical charges on the reacting constituent. Thus the equivalent weight of *di-sodium hydrogen phosphate* as an acid is $\frac{Na_2HPO_4}{1} = 142.05$; as a sodium salt is $\frac{Na_2HPO_4}{2} = 71.03$; and as a phosphate is $\frac{Na_2HPO_4}{3}, = 47.35$.

All the formulae derived under acidimetry and alkalimetry hold true for reactions of this type, and the methods of applying them are identical.

Example I.—What is the percentage of silver in a coin, if a 0.2000-gram sample requires 39.60 c.c. of potassium thiocyanate solution (0.4103 gram of KCNS per 100 c.c.) for the precipitation of the silver?

$$Ag^+ + CNS^- \rightarrow AgCNS$$

A liter of the KCNS solution contains 4.103 grams of the salt. Its normality is $\frac{\frac{4.103}{KCNS}}{1} = \frac{4.103}{97.17} = 0.04223$.

$$\frac{39.60 \times 0.04223 \times \frac{Ag}{1{,}000}}{0.2000} \times 100 = 90.20 \text{ per cent Ag.} \quad \textit{Ans.}$$

EXAMPLE II.—An impure sample of strontium chloride weighs 0.5000 gram. After adding 50 c.c. of 0.2100 N $AgNO_3$ and filtering out the precipitated silver chloride, the filtrate requires 25.50 c.c. of 0.2800 N KCNS to titrate the silver. What is the percentage of $SrCl_2$ in the sample?

Milliequivalents of $AgNO_3$ added = $50 \times 0.2100 = 10.50$.

Milliequivalents of KCNS required = $25.50 \times 0.2800 = 7.14$.

Net milliequivalents = $10.50 - 7.14 = 3.36$.

$$\text{Per cent } SrCl_2 = \frac{3.36 \times \frac{SrCl_2}{2{,}000}}{0.5000} \times 100 = 53.26 \text{ per cent.} \quad \textit{Ans.}$$

EXAMPLE III. *Liebig Method.*—How many grams of NaCN are present in a solution which is titrated just to a permanent turbidity with 26.05 c.c. of $AgNO_3$ solution containing 8.125 grams of $AgNO_3$ per liter?

$$2CN^- + Ag^+ \rightarrow Ag(CN)_2^-$$

The next drop of $AgNO_3$ gives a permanent precipitate of AgCN:

$$Ag(CN)_2^- + Ag^+ \rightarrow 2AgCN$$

$$\text{Normality of } AgNO_3 = \frac{8.125}{169.9} = 0.04782 \text{ N.}$$

The milliequivalent weight of NaCN in this case is not $\frac{NaCN}{1{,}000}$ since *two* cyanide ions react with *one* silver ion in the titration. The milliequivalent weight of NaCN may be considered here to be $\frac{2NaCN}{1{,}000}$.

Then

$$\text{Grams NaCN} = 26.05 \times 0.04782 \times \frac{2NaCN}{1{,}000} = 0.1221 \text{ gram.} \quad \textit{Ans.}$$

Or, from another point of view, if 26.05 c.c. are necessary to form the complex ion as shown above, then *twice* that amount is necessary to *precipitate* the cyanide:

$$2CN^- + 2Ag^+ \rightarrow 2AgCN.$$

Therefore

$$\text{Grams NaCN} = 2 \times 26.05 \times 0.04782 \times \frac{NaCN}{1{,}000} = 0.1221 \text{ gram.} \quad \textit{Ans.}$$

EXAMPLE IV. *Volumetric Nickel.*—How many grams of Ni are contained in an ammoniacal solution which is treated with

49.80 c.c. of KCN solution (0.007810 gram per cubic centimeter and the excess KCN titrated with 5.91 c.c. of N/10 $AgNO_3$ using KI as an indicator?

The essential reactions are:

$$Ni(NH_3)_6^{++} + 4CN^- + 6H_2O \rightarrow Ni(CN)_4^{=} + 6NH_4OH.$$

$$2CN^- + Ag^+ \rightarrow Ag(CN)_2^-$$

$$\text{Normality KCN solution} = \frac{0.007810}{\frac{\text{KCN}}{1{,}000}} = 0.1200 \text{ N}$$

$$5.91 \text{ c.c. } AgNO_3 \simeq 5.91 \times \frac{0.1000}{0.1200} \times 2 = 9.85 \text{ c.c. KCN solution (see Example III).}$$

Net cubic centimeters of KCN = 49.80 − 9.85 = 39.95 c.c.

$$39.95 \times 0.1200 \times \frac{\text{Ni}}{4{,}000} = 0.07032 \text{ gram Ni.} \quad \textit{Ans.}$$

Problems

283. What volume of 0.1233 N silver nitrate solution is required to precipitate the chloride from a sample of rock salt weighing 0.2280 gram and containing 99.21 per cent NaCl?

Ans. 31.37 c.c.

284. What volume of N/12 $BaCl_2$ solution is required to precipitate the sulphur from a solution containing 0.2358 gram of $FeSO_4.7H_2O$?

Ans. 20.36 c.c.

285. A solution of a soluble phosphate which is 0.2 N as a precipitating agent is used to precipitate the magnesium as $MgNH_4PO_4$ from a 1-gram sample of dolomite containing 14.01 per cent $MgCO_3$. What volume is required?

Ans. 16.62 c.c.

286. A solution of $K_2Cr_2O_7$ which is 0.1121 normal as an oxidizing agent is used to precipitate $BaCrO_4$ from 0.5060 gram of $BaCl_2.2H_2O$. What is the normality of the solution of $K_2Cr_2O_7$ as a precipitating agent and what volume is required?

Ans. 0.07473 N; 55.42 c.c.

287. What must be the normality of a solution of silver nitrate so that each cubic centimeter shall be equivalent to one milligram of sodium chloride? How many grams of $AgNO_3$ are contained in a liter?

Ans. 0.01710 N.
2.906 grams.

288. What is the percentage of bromine in a sample of bromide if to 1.600 grams of the sample are added 52.00 c.c. of N/5 $AgNO_3$ solution and

the excess silver requires 4.00 c.c. of N/10 KCNS solution for the precipitation of AgCNS?

Ans. 49.95 per cent.

289. What volume of oxalic acid solution which is N/5 as an acid is required to precipitate the calcium as $CaC_2O_4.H_2O$ from 0.4080 gram of cement containing 60.32 per cent CaO? What is the normality of the oxalic acid as a precipitating agent?

Ans. 43.88 c.c.; N/5.

290. A sample of feldspar contains 7.58 per cent Na_2O and 9.93 per cent K_2O. What must be the normality of a silver nitrate solution if it takes 22.71 c.c. of it to precipitate the chloride ions from the combined chlorides from a 0.1500-gram sample?

Ans. 0.03005 N.

291. In the volumetric analysis of a silver coin containing 90 per cent Ag, using a 0.5000-gram sample, what is the least normality that a potassium thiocyanate solution may have and not require more than 50 c.c. of solution in the analysis?

Ans. 0.08339 N.

292. A mixture of pure LiCl and BaI_2 weighing 0.6000 gram is treated with 45.15 c.c. of 0.2000 normal $AgNO_3$ solution and then titrated with 25.00 c.c. of N/10 KCNS solution with ferric alum as an indicator. Find the percentage of iodine present in the mixture. ($Ag^+ + CNS^- \rightarrow AgCNS$.)

Ans. 44.61 per cent.

293. A sample of greensand weighing 2.000 grams yields a mixture of NaCl and KCl weighing exactly 0.2558 gram. After dissolving the chlorides, 35.00 c.c. of 0.1 normal $AgNO_3$ are added to precipitate the chloride and the excess is titrated with 0.92 c.c. of N/50 thiocyanate solution. Calculate the percentage of potassium in the sample.

Ans. 6.36 per cent.

294. The purity of soluble iodides is determined by precipitating the iodine with an excess of standard silver nitrate and titrating the excess $AgNO_3$ with thiocyanate solution. The silver nitrate is made by dissolving 2.122 grams of metallic silver in nitric acid, evaporating just to dryness, dissolving the residue in water and diluting to exactly 1,000 c.c. Sixty cubic centimeters of this solution are added to 100 c.c. of a solution of an iodide and the excess titrated with 1.03 c.c. of thiocyanate solution of which 1 c.c. will precipitate 0.001247 gram of silver as AgCNS. Calculate the grams of iodine present as iodide in the 100-c.c. portion of the solution.

Ans. 0.1482 gram.

295. Find the per cent nickel in an ore if the sample weighs 0.3000 gram and the ammoniacal solution is treated with 20.00 c.c. of KCN (31.2 grams per liter) and then requires 14.00 c.c. of $AgNO_3$ (25.5 grams per liter) using KI as an indicator.

Ans. 26.4 per cent.

296. Find the weights of dissolved KCl, KCN, and KCNS in 500 c.c. of a solution which analyzed as follows: 30 c.c. of the solution titrated for KCN by the Liebig method reacted with 9.57 c.c. of $AgNO_3$ solution (15 grams per liter). Then 75 c.c. more of the silver solution were added and the solution was filtered. The filtrate contained enough silver to react with 9.5 c.c. of N/10 KCNS. The precipitate was heated with HNO_3 to decompose the AgCN and AgCNS, the H_2SO_4 formed was precipitated with barium nitrate and without filtering, the solution reacted with 58.4 c.c. of N/10 KCNS.

Ans. KCl = 0.85 gram.
KCN = 1.83 grams.
KCNS = 6.73 grams.

297. A solution containing KCN and KCl requires 20 c.c. of N/10 $AgNO_3$ solution to titrate the KCN to a faint turbidity by the Liebig method. After adding 50 c.c. more of the silver solution and filtering, the filtrate requires 16 c.c. of N/8 KSCN using ferric alum as an indicator. Calculate the number of millimoles of KCN and of KCl in the original solution.

Ans. 4 millimoles KCN; 1 millimole KCl.

298. A powder containing KCN, KCNS, and inert material weighs 1.200 grams and the solution of it requires 23.81 c.c. of N/12 $AgNO_3$ to titrate the KCN by the Liebig method. A 50-c.c. pipetteful of the silver solution is then added and the precipitated AgCN and AgCNS are filtered. The filtrate requires 10.12 c.c. of N/11 KCNS for the excess silver using ferric ions as the indicator. Calculate the percentage of KCN and of KCNS in the powder.

Ans. 21.53 per cent KCN.
10.21 per cent KCNS.

PART III
GAS ANALYSIS

CHAPTER XII

CALCULATIONS OF GAS ANALYSIS

56. Fundamental Laws.—Problems involving the determination of the proportional amounts of the components of a gaseous mixture, and the determination of the amount of a given substance by measuring the quantity of gas which it may be made to evolve in chemical reaction are the only phases of Gas Analysis considered in this book. The subject is not discussed at great length, and special topics such as the interpretation and calculation of flue-gas analyses are not dealt with. These topics pertain rather to chemical engineering than to general analysis, and are usually discussed in detail in books dealing with special fields of chemistry.

The calculations of gas analyses make use of the following gas laws, most of which apply strictly only to the so-called "perfect" gases, but which may be applied to ordinary analyses with results which are usually in keeping with the precision of analytical manipulation. These laws should already be more or less familiar to the student.

Boyle's Law.—The volume of a fixed mass of a gas at constant temperature is inversely proportional to the pressure to which it is subjected. That is,

$$pv = p'v' = k,$$

where pv and $p'v'$ are pairs of simultaneous values of pressure and volume of a given mass of gas, and k is a constant.

Example I.—If a sample of gas occupies a volume of 500 c.c. at a barometric pressure of 755 mm. of mercury, what volume would it occupy at a pressure of 760 mm?

An increase in pressure must cause a decrease in volume. In this case, the new volume will be:

$$500 \times \frac{755}{760} = 496.7 \text{ c.c.} \quad \textit{Ans.}$$

Or by substitution in the formula above,

$$755 \times 500 = 760 \times x,$$

whence $$x = 496.7 \text{ c.c.} \quad \textit{Ans.}$$

Charles' Law.—The volume of a fixed mass of a gas at constant pressure is directly proportional to the absolute temperature to which it is subjected; that is,

$$\frac{v}{v'} = \frac{T}{T'}$$

where vT and $v'T'$ are pairs of simultaneous values of volume and temperature expressed on the absolute scale. Zero on the absolute scale is at $-273°$C., hence the temperature in absolute units may be found by adding 273 to the temperature in Centigrade units. Charles' Law may therefore be written:

$$\frac{v}{v'} = \frac{273 + t}{273 + t'}$$

where t and t' represent the respective temperatures in degrees Centigrade.

Example II.—If a gas occupies a volume of 500 c.c. at 20°C., and the temperature is raised to 30°C. at constant pressure, what is the new volume of the gas?

The temperatures on the absolute scale are 293 and 303° respectively. If the temperature is raised, the gas must expand and the new volume becomes:

$$500 \times \frac{303}{293} = 517 \text{ c.c.} \quad \textit{Ans.}$$

Or, by substitution,

$$\frac{500}{x} = \frac{273 + 20}{273 + 30'}$$

whence, $$x = 517 \text{ c.c.} \quad \textit{Ans.}$$

The formulae expressing the above two gas laws may be combined to give

$$\frac{pv}{T} = \frac{p'v'}{T'}$$

Dalton's Law.—The pressure exerted by a mixture of gases is equal to the sum of the pressures of the individual components, and the pressure exerted by a single component is the same as the pressure that component would exert if existing alone in the same volume.

EXAMPLE III.—Moist hydrogen gas is confined over water under a pressure of 760 mm. of mercury and a temperature of 26°C. What is the actual pressure of the hydrogen?

At 26°C., the vapor pressure of water is equal to 25 mm. of mercury (see Table IV, Appendix). The partial pressure of the hydrogen is therefore 760 − 25 = 735 mm. *Ans.*

Gay Lussac's Law.—Whenever gases unite or gaseous products are formed, the proportions by volume measured at the same temperature and pressure of all the gaseous products concerned can be represented by ratios of small integers. Thus, in the reaction:

$$2H_2 + O_2 \rightarrow 2H_2O,$$

two parts by volume of hydrogen unite with *one* part by volume of oxygen to give *two* parts by volume of water vapor.

Avogadro's Law.—Equal volumes of all gases under identical conditions of temperature and pressure contain the same number of molecules.

Strictly speaking, this is a hypothesis. Increasing knowledge, however, has made this hypothesis more and more probable, until now it is usually accepted as a fundamental truth.

57. Gas-Volumetric Methods.—For convenience, Gas Analysis may be divided into the following groups:

1. Gas-volumetric methods.
2. Absorption methods.
3. Combustion methods.

Under gas-volumetric methods may be included those methods in which a gas is evolved by means of a chemical reaction, and from the volume of the gas the weight of the substance producing it is calculated.

From Avogadro's Law it is evident that the weights of equal volumes of gases will be in direct proportion to the respective molecular weights. The weight in grams of 22.4 liters of any gas, when measured under standard conditions, *i.e.*, at 0°C.

and under a pressure of 760 mm. of mercury, represents the molecular weight of the gas. If the molecular weight of a gas and the volume which a certain quantity of it occupies under standard conditions are known, the weight of that quantity may be readily determined. This is the principle underlying gas-volumetric analysis. Since it is usually inconvenient actually to measure the volume of a gas at 0°C. and under 760 mm. pressure, it is customary to measure the gas at any convenient temperature and pressure, and by means of Boyle's and Charles' Laws to calculate the volume which the gas would occupy under standard conditions.

EXAMPLE I.—A gas occupies a volume of 42.06 c.c. under 765.0 mm. pressure and at 20.0°C. What is its volume under standard conditions?

According to Boyle's Law, if the pressure of the gas at a constant temperature is reduced from 765 to 760 mm., the volume would be increased in the same ratio, and, were the temperature the same, the new volume would be

$$42.06 \times \frac{765.0}{760.0}, = 42.34 \text{ c.c.}$$

The temperature, however, is to be reduced from 20.0°C. (293° Absolute) to 0°C. (273° Absolute), and according to Charles' Law, this change alone serves to decrease the volume of the gas by the ratio of 293 to 273. If both the pressure and temperature are changed to standard conditions, the volume of the gas becomes:

$$42.06 \times \frac{765.0}{760.0} \times \frac{273.0}{293.0} = 39.45 \text{ c.c.} \quad \textit{Ans.}$$

Expressed according to the symbols used above,

$$v \times \frac{p}{p'} \times \frac{273 + t'}{273 + t} = v',$$

which is identical to the general expression:

$$\frac{pv}{T} = \frac{p'v'}{T'}$$

58. Correction for Water Vapor.—Evolved gases are frequently collected and measured over liquids which exert an appreciable vapor pressure, and in such cases the barometric pressure does not represent the pressure of the pure gas. It may be assumed that the gas will be saturated with the vapor of the liquid over which it

is measured, and in such cases the vapor pressure of the liquid depends only upon the temperature. According to Dalton's Law, the pressure of the pure gas may be found simply by subtracting the vapor pressure of the liquid at the given temperature from the barometric pressure. The values of the vapor pressure of water at different temperatures are given in Table IV, Appendix.

59. Calculations of Gas-Volumetric Analyses.—These considerations may be applied to determine the percentage of a constituent of a given substance by gas-volumetric measurements.

EXAMPLE I.—A 0.500-gram sample of limestone on treatment with acid liberates 98.7 c.c. of carbon dioxide when measured over water at 23°C. and 761 mm. pressure. What is the percentage of CO_2 in the sample?

Vapor pressure of water at 23°C. = 20.89 mm. (Table IV.)

Pressure of the pure CO_2 = 761 − 20.89 = 740 mm.

Volume of CO_2 under standard conditions =

$$98.7 \times \frac{740}{760} \times \frac{273}{273 + 23} = 88.6 \text{ c.c.} \quad \textit{Ans.}$$

The gram-molecular weight (44 grams) of CO_2 would occupy under standard conditions a volume of 22.4 liters = 22,400 c.c. The weight of CO_2 evolved is therefore:

$$44.0 \times \frac{88.6}{22{,}400} = 0.174 \text{ gram.}$$

Percentage of CO_2 in the sample is:

$$\frac{0.174}{0.500} \times 100 = 34.8 \text{ per cent.} \quad \textit{Ans.}$$

Problems

299. Three hundred cubic centimeters of hydrogen gas measured at 15°C. are heated under constant pressure to a temperature of 38.7°C. What is the increase in volume?

Ans. 24.7 c.c.

300. Five hundred cubic centimeters of hydrogen gas are cooled at constant pressure from 26 to −10°C. Calculate the volume at the new temperature.

Ans. 440 c.c.

301. The pressure on a gas which at 758 mm. occupies a volume of 600 c.c. is increased to 774 mm. at constant temperature. What is the resulting volume?

Ans. 588 c.c.

302. Two hundred and seventy-three volumes of gas at 0°C. are reduced at constant pressure to 271 volumes by lowering the temperature. What is the new temperature?

Ans. −2°C.

303. Three hundred and sixty volumes of hydrogen are measured dry at −13°C. and 760 mm. pressure. The pressure remains constant and the volume is increased 10 per cent. What is the increase in temperature?

Ans. 26°C.

304. Hydrogen is heated in a closed vessel from 0 to 100°C. The original pressure was 760 mm. What is the new pressure?

Ans. 1,038 mm.

305. One hundred grams of pure calcium carbonate are dissolved in hydrochloric acid. Calculate the volume of gas evolved when measured dry at 0°C. and 760 mm. pressure. Calculate the volume when measured dry at 15°C. and 780 mm. pressure. Calculate the volume when measured over water at 30°C. and 748 mm. barometric pressure.

Ans. 22.4 liters; 23.0 liters; 26.4 liters.

306. How many liters of oxygen gas measured over water at 16.7°C and 777 mm. pressure can be obtained from 1 kilogram of pure $KClO_3$ by ignition?

Ans. 290 liters.

307. How many cubic centimeters of hydrogen, measured over water at 22°C. and 765 mm. barometric pressure, will be formed when 0.2102 gram of sodium is thrown on water?

Ans. 112.7 c.c.

308. A quantity of hydrogen is passed over hot ferric oxide. The water formed is absorbed in a calcium chloride tube which shows an increase in weight of 1.242 grams. What was the weight of Fe_2O_3?

Ans. 3.67 grams.

309. What weight of $CaCO_3$ must be treated with acid to produce 138.6 c.c. of CO_2, measured over water (saturated with CO_2) at 10°C. and 773 mm. pressure?

Ans. 0.599 gram.

310. If in the analysis of a 0.3000-gram sample of a carbonate, 18.00 c.c. of CO_2, measured over water saturated with CO_2 at 18°C. and 760 mm. barometric pressure, were obtained, find the percentage of carbon present in the carbonate.

Ans. 2.96 per cent.

311. In the analysis of dolomite, 0.0500 gram of ferric oxide, 0.6080 gram of CaO and 0.1505 gram of magnesium pyrophosphate were obtained. If these were originally present as $FeCO_3$, $CaCO_3$, and $MgCO_3$, how many

cubic centimeters of CO_2 measured dry at 20°C. and 780 mm. pressure could have been obtained from the same weight of sample?

Ans. 300.3 c.c.

312. What weight of silicate should be taken for analysis such that the number of cubic centimeters of water vapor evolved on heating, and measured at 150°C. and 760 mm. pressure, is equal to 100 times the per cent hydrogen present?

Ans. 0.577 gram.

313. What weight of limestone should be taken for analysis such that the volume in cubic centimeters of CO_2 measured dry at 20°C. and 780 mm. equals the percentage of CO_2 present?

Ans. 0.1880 gram.

314. The calcium in a sample of dolomite weighing 0.9380 gram is precipitated as calcium oxalate, dried, and ignited to calcium oxide. If 56.83 c.c. of gas measured dry at 764 mm. and 20°C. are evolved on ignition, what is the percentage of CaO in the dolomite?

Ans. 7.10 per cent.

315. A sample of pyrite (FeS_2) weighing 0.2000 gram yields 0.7783 gram of $BaSO_4$. How many cubic feet of air measured at 130°F. and 27 inches of mercury pressure would theoretically be required to burn 1 pound of the pyrite? What would be the volume of the gaseous residue (sulphur dioxide and residual nitrogen) measured at the same temperature and pressure? ($4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$) (Air = 20.9 per cent O_2 by volume).

Ans. 52.4 cu. ft.
51.8 cu. ft.

316. A compound which may be either di-methyl aniline ($C_6H_5N(CH_3)_2$) or di-ethyl aniline ($C_6H_5N(C_2H_5)_2$), on decomposition is found to yield a volume of nitrogen (measured dry at 27°C. and 760 mm. pressure) which when expressed in cubic centimeters is approximately equal to 100 times the weight in grams of the sample taken. What was the compound taken?

Ans. Di-methyl aniline.

317. Compute the volume of H_2O which can be obtained from 8 grams of $H_4Ca_{12}Al_6S_{10}O_{43}$ measured at (*a*) 20°C. and 750 mm. pressure and (*b*) at 750 mm. pressure and 900°C. (2 significant figures.)

Ans. (*a*) 0.18 c.c.
(*b*) 970 c.c.

318. A sample of dolomite is found to contain insoluble matter, 1.80 per cent Fe_2O_3, 13.00 per cent MgO, and 38.15 per cent CaO. Using a 1-gram sample, a student analyzes for CO_2 and obtains 260.0 c.c. of gas when measured over water saturated with CO_2 at 20°C. and 750 mm. pressure. If iron, magnesium, and calcium were present wholly as $FeCO_3$, $MgCO_3$, and $CaCO_3$, what percentage error was made in the CO_2 determination?

Ans. 1.6 per cent.

60. Absorption Methods.—Absorption methods of Gas Analysis apply to the determination of the proportionate amounts of the components of a gaseous mixture. The mixture of gases is treated with a series of absorbents and the temperature and pressure are usually kept constant throughout the entire determination. In cases where these are allowed to vary, corrections for their effect may be made by applying the principles outlined in Sec. 56. The difference in the volume of the gas before and after it has been acted upon by each absorbing agent represents the amount of gas absorbed, and the amount is usually expressed on a percentage-by-volume basis. The many forms of apparatus used for carrying out gas absorptions are described in the textbooks on the subject, but the fundamental principles are identical. The reagents commonly employed are listed below:

Gas	Reagent
Carbon dioxide	Caustic soda Caustic potash
Unsaturated hydrocarbons ("Illuminants")	Bromine water Fuming sulphuric acid
Oxygen	Alkaline pyrogallol solution Yellow phosphorus
Carbon monoxide	Ammoniacal cuprous chloride
Hydrogen	Palladium sponge Palladous chloride solution Colloidal palladium solution.

Example I.—A sample of illuminating gas occupying a volume of 80.0 c.c. is treated in succession with caustic potash solution, fuming sulphuric acid, alkaline pyrogallol solution, and ammoniacal cuprous chloride solution. After each treatment, the volume of the residual gas at constant temperature and pressure is measured as 78.7,75.5,75.1 and 68.3 c.c., respectively. What is the percentage composition of the gas as shown by these results?

$$\text{Volume of } CO_2 = 80.0 - 78.7 = 1.3 \text{ c.c.}$$
$$\text{Volume of illuminants} = 78.7 - 75.5 = 3.2 \text{ c.c.}$$
$$\text{Volume of } O_2 = 75.5 - 75.1 = 0.4 \text{ c.c.}$$
$$\text{Volume of CO} = 75.1 - 68.3 = 6.8 \text{ c.c.}$$

The percentages of the various components are therefore:

$$\left.\begin{aligned}
&\frac{1.3}{80.0} \times 100 = 1.6 \text{ per cent } CO_2 \\
&\frac{3.2}{80.0} \times 100 = 4.0 \text{ per cent illuminants} \\
&\frac{0.4}{80.0} \times 100 = 0.5 \text{ per cent } O_2 \\
&\frac{6.8}{80.0} \times 100 = 8.5 \text{ per cent CO.} \\
&\frac{68.3}{80.0} \times 100 = 85.4 \text{ per cent inert gases}
\end{aligned}\right\} \textit{Ans.}$$

61. Combustion Methods.—If a gas mixture contains one or more components capable of combustion with oxygen, it is usually possible to determine the percentage of these components by allowing combustion to take place, and measuring either the contraction in volume, the amount of carbon dioxide formed, the volume of oxygen used, or combinations of these measurements, depending upon the number and character of the combustible components present. Gay Lussac's Law underlies calculations involving contractions in volume. Thus, in the combustion of carbon monoxide with oxygen:

$$2CO + O_2 \rightarrow 2CO_2,$$

two volumes of carbon monoxide unite with *one* volume of oxygen to form *two* volumes of carbon dioxide. The combustion is therefore accompanied by a contraction equal to one-half the volume of the carbon monoxide present and produces a volume of carbon dioxide equal to the original volume of carbon monoxide.

Assume a gas mixture with hydrogen and methane as the only combustible components. Hydrogen reacts with oxygen according to the equation:

$$2H_2 + O_2 \rightarrow 2H_2O,$$

in which *two* volumes of hydrogen unite with *one* volume of oxygen to form water vapor, condensing at ordinary temperatures to liquid water. Methane reacts with oxygen according to the equation:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O,$$

in which *one* volume of methane reacts with *two* volumes of

oxygen to form *one* volume of carbon dioxide. Let x represent the volume of hydrogen, and y the volume of methane present in the gas mixture. The volume of oxygen required for the hydrogen is $\frac{1}{2}x$, and the volume of oxygen required for the methane is $2y$. The total volume of oxygen required, B, is therefore given by the expression:

$$(1) \qquad B = \tfrac{1}{2}x + 2y.$$

The contraction in volume caused by the hydrogen reaction is $\frac{3}{2}x$, and that by the methane reaction is $2y$. The total contraction in volume, C, is given by the expression:

$$(2) \qquad C = \tfrac{3}{2}x + 2y,$$

whence,

$$x = C - B = \text{volume of hydrogen},$$

$$y = \frac{3B - C}{4} = \text{volume of methane}.$$

It is evident that by allowing this gas mixture to react with a determinable volume of oxygen, and measuring the resulting contraction which the gas undergoes, it is possible to determine the volume of hydrogen and methane present.

Since carbon dioxide is appreciably soluble in water, it is customary in accurate analyses to measure the contraction in volume after the carbon dioxide has been entirely absorbed. Under such conditions, in the combustion of a mixture of hydrogen and methane the volume of oxygen required would be represented as before by the equation:

$$(1) \qquad B = \tfrac{1}{2}x + 2y,$$

but the total decrease in volume due to *combustion and absorption* would be

$$(2) \qquad C' = \tfrac{3}{2}x + 3y,$$

whence

$$x = \tfrac{4}{3}C' - 2B = \text{volume of hydrogen},$$
$$y = B - \tfrac{1}{3}C' = \text{volume of methane}.$$

Instead of measuring the contraction in volume and the oxygen consumed, the amounts of hydrogen and methane present in a mixture in which they are the only combustible components may be determined from the contraction in volume and the volume of carbon dioxide produced by combustion. Com-

bustion of hydrogen of volume x causes a contraction in volume of $\frac{3}{2}x$ and produces no carbon dioxide; combustion of methane of volume y causes a contraction of $2y$ and produces a volume of carbon dioxide equal to y. The total contraction in volume C is therefore given by the equation:

$$C = \tfrac{3}{2}x + 2y,$$

and the total volume of carbon dioxide produced D is given by:

$$D = y.$$

Hence,

$$x = \frac{2C - 4D}{3} = \text{volume of hydrogen},$$

$$y = D = \text{volume of methane}.$$

In a similar way, the percentage composition of other mixtures of gases may usually be calculated, provided as many independent equations can be formulated as there are unknown components in the mixture.

The following equations represent combustion reactions more commonly encountered in Gas Analysis, and the accompanying table shows the volume relationships in each case.

	Vol. gas	O_2 consumed	Contraction	CO_2 produced
Hydrogen $2H_2 + O_2 \rightarrow 2H_2O$	1	½	1½	0
Carbon monoxide $2CO + O_2 \rightarrow 2CO_2$	1	½	½	1
Methane $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	1	2	2	1
Acetylene $2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$	1	2½	1½	2
Ethylene $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$	1	3	2	2
Ethane $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$	1	3½	2½	2
Propylene $2C_3H_6 + 9O_2 \rightarrow 6CO_2 + 6H_2O$	1	4½	2½	3
Propane $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$	1	5	3	3
Butane $2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O$	1	6½	3½	4

With this table, little difficulty should be experienced in formulating the necessary equations for the determination by combustion of any mixture of the gases.

In case air is used for combustion, it may be assumed to consist of 20.9 per cent of oxygen by volume.

EXAMPLE I.—A mixture of carbon monoxide and nitrogen occupies a volume of 100 c.c. and on combustion with oxygen

produces 40 c.c. of carbon dioxide. Calculate the percentage of nitrogen in the mixture.

Let x represent the volume of carbon monoxide and y the volume of nitrogen. Since one volume of carbon monoxide on combustion gives one volume of carbon dioxide, the volume of carbon dioxide produced is equal to x. This volume is stated to be 40 c.c., and the volume of nitrogen is therefore 60 c.c. N_2 = 60 per cent. *Ans.*

Example II.—A mixture of carbon monoxide, methane, and nitrogen occupies a volume of 20 c.c. On combustion with an excess of oxygen, a contraction of 21 c.c. takes place, and 18 c.c. of carbon dioxide are formed. What is the volume of each component in the mixture?

Let x = volume of CO,
y = volume of CH_4,
z = volume of N_2.

Total contraction in volume, $C = \frac{1}{2}x + 2y$.

Total volume of CO_2 produced, $D = x + y$.

$$x = \frac{4D - 2C}{3} = \frac{72 - 42}{3} = 10 \text{ c.c.}$$

$$y = \frac{2C - D}{3} = \frac{42 - 18}{3} = 8 \text{ c.c.}$$

z = volume original gas $- (x + y) = 2$ c.c.

Ans.

Example III.—The residual gas mentioned in Example I, Sec. 60, is assumed to consist entirely of hydrogen, methane, and nitrogen. To a 20.0-c.c. sample are added exactly 100.0 c.c. of air, and the mixture is exploded. After the carbon dioxide is absorbed in caustic potash, the volume of the gas is found to be 88.0 c.c., and after the excess oxygen is absorbed in pyrogallol, the volume of the gas is 82.1 c.c. What is the percentage of each component in the gas mixture and in the original illuminating gas?

Volume after adding air = 120 c.c.

Contraction after explosion and absorption = 120 − 88.0 = 32.0 c.c. = C'.

Volume of oxygen taken = 100.0 × 0.209 = 20.9 c.c.

Volume of residual oxygen = 88.0 − 82.1 = 5.9 c.c.

Oxygen actually required = 20.9 − 5.9 = 15.0 c.c. = B.

Substituting these values of B and C' in the equations derived above, namely,

$$x = \tfrac{4}{3}C' - 2B,$$
$$y = B - \tfrac{1}{3}C',$$

the results obtained are:

$x = (\tfrac{4}{3} \times 32.0) - (2 \times 15.0) = 12.7$ c.c. = volume hydrogen,
$y = 15.0 - (\tfrac{1}{3} \times 32.0) = 4.3$ c.c. = volume methane,
$20.0 - (12.7 + 4.3) = 3.0$ c.c. = volume nitrogen.

The percentages by volume of these components are found by dividing these volumes by 20.0 and multiplying by 100.

63.5 per cent H_2
21.5 per cent CH_4 } *Ans.*
15.0 per cent N_2

In the original illuminating gas (Example I, Sec. 60) the percentages of these components are:

$$12.7 \times \frac{68.3}{20.0} \times \frac{100}{80.0} = 54.2 \text{ per cent } H_2$$
$$4.3 \times \frac{68.3}{20.0} \times \frac{100}{80.0} = 18.3 \text{ per cent } CH_4 \quad \} \textit{Ans.}$$
$$3.0 \times \frac{68.3}{20.0} \times \frac{100}{80.0} = 12.8 \text{ per cent } N_2$$

Problems

319. The following measurements are made under identical conditions. Calculate the percentages of CO_2, O_2, CO, and N_2 in a sample of gas containing no other components:

Sample taken	100.0 c.c.
Volume after KOH treatment	91.5 c.c.
Volume after pyrogallol treatment	81.4 c.c.
Volume after cuprous chloride treatment	81.1 c.c.

Ans. $CO_2 = 8.5$ per cent.
$O_2 = 10.1$ per cent.
$CO = 0.3$ per cent.
$N_2 = 81.1$ per cent.

320. The following measurements are made under identical conditions. Calculate the percentages of carbon dioxide, oxygen, carbon monoxide, and nitrogen in a sample of gas containing no other components:

Sample taken	79.5 c.c.
Volume after KOH treatment	72.9 c.c.
Volume after O_2 absorption	64.6 c.c.
Volume after CO absorption	64.5 c.c.

Ans. CO_2 = 8.3 per cent.
O_2 = 10.4 per cent.
CO = 0.1 per cent.
N_2 = 81.2 per cent.

321. How many liters of oxygen are necessary for the complete combustion of 5 liters of (*a*) methane; (*b*) acetylene; (*c*) hydrogen sulphide?

Ans. (*a*) 10 liters; (*b*) 12.5 liters; (*c*) 7.5 liters.

322. The following measurements are made under identical conditions. Calculate the percentage composition of a mixture of hydrogen and nitrogen:

Volume of gas taken	58.2 c.c.
Volume of oxygen added	32.0 c.c.
Volume of oxygen consumed by combustion	6.1 c.c.

Ans. H_2 = 21.0 per cent.
N_2 = 79.0 per cent.

323. The following measurements are taken under identical conditions. Calculate the percentage composition of a mixture of hydrogen and nitrogen:

Volume of gas taken	95.3 c.c.
Volume of oxygen added	40.8 c.c.
Volume of gas after combustion	40.1 c.c.

Ans. H_2 = 67.2 per cent.
N_2 = 32.8 per cent.

324. What is the percentage composition of a mixture of hydrogen and nitrogen if the contraction in volume due to combustion with oxygen is the same as the volume of the sample taken?

Ans. H_2 = 66⅔ per cent.
N_2 = 33⅓ per cent.

325. What is the percentage of methane in a mixture of hydrogen, methane, and acetylene if 16.0 c.c. of the mixture when exploded with an excess of air cause a contraction of 26.0 c.c.?

Ans. 25.0 per cent.

326. The following measurements are made under identical conditions. Calculate the percentage composition of a mixture of hydrogen, carbon monoxide, and methane:

Volume of gas taken	10.5 c.c.
Volume of air added	137.4 c.c.
Total volume after combustion	136.1 c.c.
Volume after removing CO_2	129.6 c.c.

Ans. H_2 = 38.1 per cent.
CO = 45.7 per cent.
CH_4 = 16.2 per cent.

327. What is the percentage of propane in a mixture of propane, carbon monoxide, and methane if a 13.7-c.c. sample on combustion produces 23.7 c.c. of carbon dioxide?

Ans. 36.5 per cent.

328. What is the percentage composition of a mixture of carbon monoxide, ethane, and nitrogen, if on combustion with oxygen, the contraction in volume and the volume of carbon dioxide produced are each numerically equal to the volume of the sample taken?

Ans. CO = 33⅓ per cent.
C_2H_6 = 33⅓ per cent.
N_2 = 33⅓ per cent.

329. To 40.8 c.c. of a mixture of hydrogen, nitrogen, and carbon monoxide are added 150.0 c.c. of air, and the mixture is exploded. If 4.8 c.c. of CO_2 are produced and the residual oxygen requires 42.0 c.c. of hydrogen for combustion, what is the percentage composition of the original mixture, and what was the total volume after the first combustion?

Ans. H_2 = 39.0 per cent.
N_2 = 49.3 per cent.
CO = 11.7 per cent.
Volume = 164.6 c.c.

330. What is the percentage composition of a mixture of hydrogen, carbon monoxide, and methane if the volume of the oxygen consumed in combustion and the volume of the carbon dioxide produced are each equal to three-fourths of the volume of the original gas taken?

Ans. H_2 = 25 per cent.
CO = 58⅓ per cent.
CH_4 = 16⅔ per cent.

331. From the following data calculate the percentage composition of a sample of illuminating gas known to contain the components given below:

Sample taken for analysis	100.6 c.c.
Volume after KOH treatment	98.4 c.c.
After Br_2 treatment	94.2 c.c.
After pyrogallol treatment	93.7 c.c.
After Cu_2Cl_2 treatment	85.2 c.c.
Residual gas taken for analysis	10.3 c.c.
Volume of air added	87.3 c.c.
Volume after explosion	80.1 c.c.
Carbon dioxide produced	5.2 c.c.

Ans. CO_2 = 2.2 per cent.
Unsaturated compounds = 4.2 per cent.
O_2 = 0.5 per cent.
CO = 8.4 per cent.
CH_4 = 42.8 per cent.
H_2 = 38.6 per cent.
N_2 = 3.3 per cent.

332. A known volume of a mixture of methane, carbon monoxide, and nitrogen is exploded with an excess of air. Show by equations that the percentage composition of the mixture cannot be determined by measuring the contraction in volume and the volume of oxygen consumed.

PART IV
POTENTIOMETRIC ANALYSIS

CHAPTER XIII

ELECTROMETRIC TITRATIONS

62. Electromotive Series.—If a piece of zinc is placed in contact with water or with a dilute solution of zinc ions, some of the zinc will dissolve and form zinc ions: $Zn - 2\epsilon \rightarrow Zn^{++}$. This transfer of electrons leaves the metal negatively charged and the solution positively charged. In other words, a difference of potential is set up between the metal and the solution. This electromotive force, in part, tends to reverse this process so that equilibrium is very quickly reached and the action soon ceases.

If a piece of copper is placed in contact with water or with a very dilute solution of copper ions, a similar action takes place, but the tendency for the metal to dissolve is much less than in the case of the zinc. In contact with a more concentrated solution of copper ions, copper will plate out from the solution giving the metal electrode a positive charge. Again an electromotive force is set up which opposes this process and the action soon stops.

Neither of the above cases provides a permanent source of electricity, but if the zinc (in contact with its ions) is connected to the copper (in contact with its ions) and the solutions are connected through a porous wall or by means of a salt-bridge, equilibrium will be continually destroyed and a current will flow in the outer circuit from the copper to the zinc, and in the solution from the zinc to the copper. This is the principle of the Daniell cell. The reaction is obviously one of oxidation and reduction. The metallic zinc is oxidized (increases in positive valence); the copper ions are reduced (decrease in positive valence). The voltage of this current is a measure of the *relative* electrolytic solution pressures or tendencies to ionize of the two metals. Relative values can therefore be tabulated for these and

other oxidation-reduction reactions, and the so-called *electromotive series* is such a tabulation. In it the difference of potential between hydrogen gas and a one molal solution of hydrogen ions is arbitrarily taken as zero, and the tabulated values are the *relative* potentials between metals and one molal solutions of their ions. The following are a few important values in the electromotive series:

Element	Volts	Element	Volts
$K^\circ - K^+$	+2.93	$Cu^+ - Cu^{++}$	−0.17
$Na^\circ - Na^+$	+2.72	$As^\circ - As^{+++}$	−0.29
$Ca^\circ - Ca^{++}$	+2.60	$Cu^\circ - Cu^{++}$	−0.34
$Al^\circ - Al^{+++}$	+1.30	$Co^\circ - Co^{+++}$	−0.40
$Zn^\circ - Zn^{++}$	+0.76	$Cu^\circ - Cu^+$	−0.51
$Fe^\circ - Fe^{++}$	+0.43	$2I^- - I_2$	−0.53
$Cd^\circ - Cd^{++}$	+0.40	$Fe^{++} - Fe^{+++}$	−0.75
$Ni^\circ - Ni^{++}$	+0.22	$Ag^\circ - Ag^+$	−0.80
$Pb^\circ - Pb^{++}$	+0.12	$Hg^\circ - Hg^{++}$	−0.86
$Sn^\circ - Sn^{++}$	+0.10	$2Br^- - Br_2$	−1.08
$Fe^\circ - Fe^{+++}$	+0.04	$2Cl^- - Cl_2$	−1.35
$H_2 - 2H^+$	0.00	$Pb^{++} - PbO_2$	−1.44
$Sb - Sb^{+++}$	−0.10	$Co^{++} - Co^{+++}$	−1.86
$Sn^{++} - Sn^{++++}$	−0.14	$2F^- - F_2$	−1.96

The physicist who is more interested in the current in the outer conductor considers the potential of copper to be greater than that of zinc; the chemist who is interested in the changes within the solution considers the potential of zinc to be greater than that of copper. The numerical values in the series given above are from the point of view of the chemist (*reduction potential series*). By changing the sign of each value, the table is converted to an *oxidation potential series.*

EXAMPLE I.—What is the E. M. F. of a Daniell cell in which the solutions are each one molal?

Reduction potential of $Zn - Zn^{++}$ (1 molal) = +0.76 volt.
Reduction potential of $Cu - Cu^{++}$ (1 molal) = −0.34 volt.
E. M. F. of cell = (+0.76) − (−0.34) = 1.10 volts. *Ans.*

The electromotive series is of value in predicting and correlating chemical changes. Since the table shows the relative tendency of elements to increase and decrease in valence, the

elements in the upper left-hand column are the stronger reducing agents and those in the lower right-hand column are the stronger oxidizing agents. For example, metallic zinc will reduce H^+ to H° and Cu^{++} to Cu°, and when present together, the latter reduction will take place first, since copper has less tendency to be oxidized and therefore greater tendency to plate out. That is, zinc will cause the deposition of copper from a cupric solution even when acid is present. Conversely, hydrogen ions will oxidize metallic zinc but will not oxidize copper. That is, copper will not dissolve in an acid like HCl. (It dissolves in HNO_3 only because of the oxidizing action of the nitrate radical.) Electrolysis of a solution of brass will cause deposition of copper and lead (as PbO_2) and not of zinc so long as the solution remains acid and overvoltage effects are avoided, for the current at the cathode will reduce H^+ in preference to Zn^{++}.

63. Nernst Formula.—A general formula which expresses the value of the actual potential difference between a metal and a solution of its ions was derived by Nernst from theoretical considerations and is as follows:

$$E = \frac{RT}{NF} \log_e \frac{P}{p}$$

in which

E = potential difference in volts.
R = gas constant = 8.32.
F = faraday = 96,500.
N = valence change of the element.
P = electrolytic solution pressure.
p = osmotic pressure of the ions.
T = absolute temperature.

By substituting the known values of R and F, converting to common logarithms, and assuming the temperature to be 18°C., the formula becomes much more simple:

$$E = \frac{0.058}{N} \log \frac{P}{p}.$$

The Nernst formula was derived from the laws of so-called "perfect" solutions and applies strictly only to such solutions. It applies however with fair approximation to all solutions in

which the solute is present at low concentration. Since in such solutions the value for p is proportional to the concentration of the solution, the Nernst formula shows that the difference of potential between a metal and its ions depends upon the concentration of the ions in the solution. The less the concentration, the greater the potential difference. If two electrodes of the same metal are placed in contact with solutions of its ions of two different concentrations and a circuit is made, the metal will plate out from the more concentrated solution and dissolve from the electrode in the more dilute solution. A current will therefore flow in the outer circuit from the electrode in contact with the solution of greater concentration to the electrode in contact with the less concentrated solution. Such a cell involving only one metal is called a *concentration cell.*

Assume such a concentration cell to consist of a metal in contact with solutions of its ions of concentrations C_1 and C_2. The Nernst formula shows that the differences of potential between the metal and the solutions are respectively

$$E_1 = \frac{0.058}{N} \log \frac{P}{p_1},$$

and

$$E_2 = \frac{0.058}{N} \log \frac{P}{p_2}.$$

The E. M. F. or potential difference of the cell is therefore

$$E = E_1 - E_2 = \frac{0.058}{N} \left(\log \frac{P}{p_1} - \log \frac{P}{p_2} \right)$$
$$= \frac{0.058}{N} \log \frac{p_2}{p_1}.$$

Since the values p_1 and p_2 are approximately proportional to concentration,

$$E = \frac{0.058}{N} \log \frac{C_2}{C_1}.$$

Example I.—What is the E. M. F. of the concentration cell: Ag, Ag^+ (0.01 normal) — Ag, Ag^+ (0.00001 normal)?

$$E = \frac{0.058}{1} \log \frac{0.01}{0.00001}$$
$$= 0.058 \times 3 = 0.174 \text{ volt.} \quad Ans.$$

EXAMPLE II.—What is the E. M. F. of the cell: Zn, Zn^{++} (0.1 molal) — Cu, Cu^{++} (0.001 molal)?

Reduction potential Zn, Zn^{++} (1 molal) = +0.76 volt.
Reduction potential Zn, Zn^{++} (0.1 molal)

$$= +0.76 + \frac{0.058}{2} \log \frac{1}{0.1} = +0.79 \text{ volt.}$$

Reduction potential Cu, Cu^{++} (1 molal) = −0.34 volt.
Reduction potential Cu, Cu^{++} (0.001 molal)

$$= -0.34 + \frac{0.058}{2} \log \frac{1}{0.001} = -0.25 \text{ volt.}$$

E. M. F. of cell = (+0.79) − (−0.25) = 1.04 volts. *Ans.*

EXAMPLE III.—If a piece of iron is immersed in a dilute solution of cupric ions, the iron dissolves and the copper precipitates out. Assuming that the resulting solution is one molal in ferrous ions, what will be the approximate concentration of cupric ions remaining in solution?

Fe, Fe^{++} (1 molal) = +0.43 volt.
Cu, Cu^{++}(1 molal) = −0.34 volt.

Copper will continue precipitating out until its concentration in solution is such that the reduction potential of Cu, Cu^{++} is raised to +0.43 volt.

$$E_1 - E_2 = 0.43 - (-0.34) = 0.77 \text{ volt.}$$

$$0.77 = \frac{0.058}{2} \log \frac{1}{x}$$

$$x = 2.8 \times 10^{-27} \text{ molal.} \quad \textit{Ans.}$$

64. Application of Nernst Formula to Electrometric Titrations. As shown in Example I above, the E. M. F. of a concentration cell can be calculated by means of the Nernst formula from the values of the two concentrations. Similarly, if one concentration and the E. M. F. of the cell are known, the other concentration can be calculated.

Suppose a concentration cell consists of a hydrogen electrode (platinum black saturated with hydrogen gas) immersed in a solution of known hydrogen-ion concentration (for example 1 molal) and of a hydrogen electrode immersed in a solution of hydrogen ions the concentration (*i.e.*, the "acidity") of which is desired.

Connecting the electrodes with wire and the solutions with a salt-bridge, a current will flow through the wire and its voltage can be measured. Suppose in this case the E. M. F. is found to be 0.205 volt. Then

$$E = 0.205 = \frac{0.058}{N} \log \frac{C_1}{C_2}$$
$$= \frac{0.058}{1} \log \frac{1}{C_2}$$
$$C_2 = 0.00029.$$

The solution is therefore 0.00029 molal.

In actual practice it is not convenient to use as a standard a hydrogen electrode in one molal hydrogen-ion solution. Instead, a calomel cell is usually used which consists of metallic mercury in contact with a solution saturated with mercurous chloride and normal with respect to potassium chloride. The potential of this cell differs from that of hydrogen against 1 molal hydrogen ions by 0.285 volt. This calomel cell is connected to the solution the hydrogen-ion concentration of which is desired through a salt-bridge consisting of a concentrated solution of potassium chloride. The E. M. F. of the current in this case is

$$E = 0.285 + \frac{0.058}{1} \log \frac{1}{C},$$

whence,

$$\log C = -\frac{E - 0.285}{0.058}.$$

65. P_H Value.—Hydrogen-ion concentrations are often given in terms of so-called "P_H values." The P_H value of a solution is the logarithm of the reciprocal of the concentration of hydrogen ions:

$$P_H = \log \frac{1}{C} = -\log C.$$

The P_H value of a solution which is 10^{-5} normal in hydrogen ions is $\log \frac{1}{10^{-5}} = 5$. In the above case with the standard calomel cell,

$$P_H = \frac{E - 0.285}{0.058}$$

$$pH = \frac{E - .281}{.059}$$

66. Electrometric Titration Apparatus.—The essential parts to an electrometric titration apparatus are shown in the accompanying diagram. An outer circuit consists of a dry cell C, a rheostat R, and a voltmeter V. The resistance R is varied until no deflection of the galvanometer G is observed when the key K is momentarily closed. This indicates that the voltage of the outer (dry cell) circuit as read from the voltmeter is equal to that of the inner circuit as given by the solution.

If desired the voltmeter may be modified so as to read concentration values or P_H values directly. As a matter of fact in an ordinary titration the actual values of voltage or concentration are usually of little value in themselves except as a means of establishing the end point of the neutralization. If in an acidimetric process the voltage of the solution is measured after the addition of each small increment of titrating solution and these voltages are plotted graphically against the corresponding total volume of titrating solution, a curve will be given which "inflects" suddenly at the point of neutralization. The volume corresponding to the midpoint of this inflection is the volume of titrating solution corresponding to the end point of the neutralization. Incidentally, with a strong acid against a strong base the hydrogen-ion concentration of the solution at the end point will be that of pure water, or 10^{-7} ($P_H = 7$); with a weak acid against a strong base the hydrogen-ion concentration will be less than 10^{-7}; with a strong acid against a weak base it will be greater than 10^{-7} (see Sec. 46).

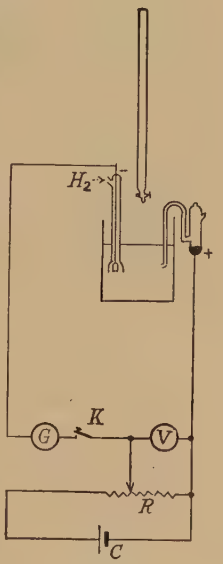


FIG. 1.

EXAMPLE I.—The electrometric titration of solutions containing (*a*) hydrochloric acid, and (*b*) acetic acid, with tenth normal sodium hydroxide solution gave values for the voltages of the solutions which when plotted against the volumes of base added gave the accompanying graph. How many grams (*a*) of HCl, and (*b*) of $HC_2H_3O_2$ were present, and what was the P_H value at the end point in each case?

The point on the graph corresponding to the end point in each case is found by bisecting the nearly vertical part of the curve. This corresponds in curve **A** to 20.0 c.c. and 0.70 volt; in curve **B** to 20.0 c.c. and 0.76 volt.

(*a*) Grams HCl $= 20.0 \times 0.1 \times 0.0365 = 0.0730$ gram.

$$P_H \text{ value} = \frac{0.70 - 0.285}{0.058} = 7.1$$

(*b*) Grams $HC_2H_3O_2 = 20.0 \times 0.1 \times 0.060 = 0.120$ gram.

$$P_H \text{ value} = \frac{0.76 - 0.285}{0.058} = 8.1 \qquad \textit{Ans.}$$

67. Oxidation and Reduction Titrations.—Electrometric titrations may be applied to oxidation and reduction reactions as

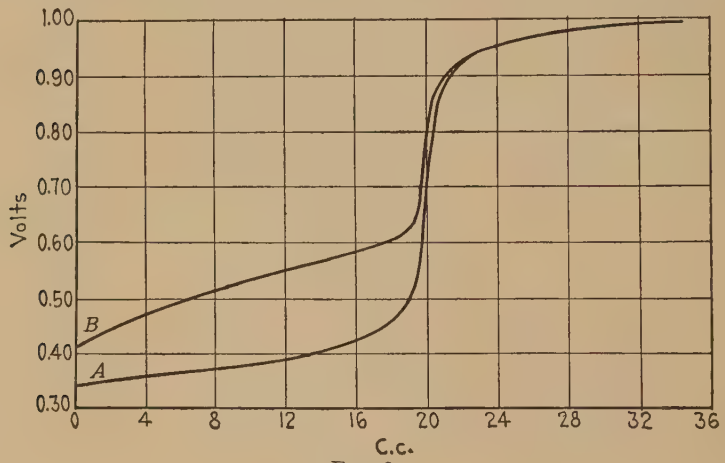


FIG. 2.

well as to acidimetric reactions. In the latter case it was found that a difference of potential exists between hydrogen gas and a solution containing hydrogen ions, which is the oxidation product of hydrogen ($H - \epsilon \rightarrow H^+$). Similarly, a potential difference exists between ferrous and ferric ions ($Fe^{++} - \epsilon \rightarrow Fe^{+++}$). As in the case of the hydrogen concentration cell, if two solutions each containing ferrous and ferric ions but at different relative concentrations are connected internally by means of a salt-bridge and externally by means of a platinum wire, a current will flow through the wire. In one solution the ferrous ions will

have a relatively greater tendency to give a negative charge to the electrode (*i.e.*, give up electrons to the wire) and in the other solution the ferric ions will have a relatively greater tendency to give a positive charge to the electrode (*i.e.*, take up electrons from the wire). The current will flow though the wire from the solution of greater concentration of ferric ions to the solution of lesser concentration of ferric ions. As in the case of the hydrogen concentration cells the passage of electrons will tend to cause equalization of the relative concentrations of the two solutions.

The Nernst formula applied to the ferrous-ferric-ion cell shows that its potential is

$$E = \frac{0.058}{1} \log \frac{Fe^{++} / Fe^{+++}}{Fe_1{}^{++} / Fe_1{}^{+++}}.$$

If one of the solutions is taken as a standard and the relative concentration of ferrous ions to ferric ions $Fe_1{}^{++}/Fe_1{}^{+++}$ is made unity, then the potential is

$$E = 0.058 \log \frac{Fe^{++}}{Fe^{+++}}.$$

It is inconvenient to use as the standard a known ferrous-ferric-ion equilibrium. Instead, the calomel cell is used as in acidimetric titrations. Its potential differs from that of the potential between ferrous and ferric ions of equal concentrations by 0.47 volt. The Nernst formula in this case therefore becomes

$$E = 0.47 + 0.058 \log \frac{Fe^{++}}{Fe^{+++}}.$$

If the E. M. F. is measured, the relative concentrations of ferrous and ferric ions may therefore be calculated.

Inspection of this formula shows that in the titration of a ferrous salt with, for example, potassium dichromate, the ratio of concentration of ferrous ions to ferric ions will change during the process of the titration. The measured value of E will likewise slowly change. Only when the end point is approximated and the concentration of ferrous ions becomes nearly zero will there be a very sudden change in E. This change is so abrupt that in oxidation titrations it is usually unnecessary to tabulate the values for the E. M. F. in order to determine the volume of titrating solution corresponding to a sudden break in the curve. The titrating solution is added in small increments until the

voltmeter shows a very sudden deflection and the volume is read directly from the burette.

Electrometric titrations may of course be applied to oxidation reactions other than ferrous ions to ferric ions. The coefficient for the calomel electrode is different for different oxidation reactions, but the sudden change in voltage at the end point is common to all. When the voltage is plotted graphically against volumes as abscissae, the end point is found by bisecting the nearly vertical part of the curve, as in acidimetric titrations.

Problems

333. Will metallic lead precipitate tin from a neutral solution of a stannous salt? Will lead precipitate tin from an acid solution of a stannous salt?

Ans. Yes. No.

334. How many grams of cadmium can remain dissolved in a liter of a neutral solution which is molal in ferrous ions and is in contact with metallic iron? How many grams of copper?

Ans. 10.4 grams; 1.79×10^{-25} gram.

335. What is the E. M. F. of the cell Zn, Zn^{++} (0.001 molal) — Cu, Cu^{++} (0.1 molal)?

Ans. 1.16 volts.

336. What is the E. M. F. of the concentration cell Ag, Ag^{+} (0.01 molal) — Ag, Ag^{+} (0.00001 molal)?

Ans. 0.174 volt.

337. What is the E. M. F. of the following concentration cell: Ag, 0.1N $AgNO_3$ solution (80 per cent ionized) — Ag, saturated AgI solution if the solubility of AgI is 2.35×10^{-6} gram per liter and its ionization is 100 per cent?

Ans. 0.400 volt.

338. The more concentrated solution of a hydrogen concentration cell consists of 0.08 normal HCl solution (85 per cent ionized). The E. M. F. of the cell is 0.100 volt. What is the hydrogen-ion concentration and P_H value of the other solution?

Ans. 1.29×10^{-3} normal; 2.89.

339. A hydrogen electrode and a calomel electrode in contact with a dilute acid solution at 18°C. show a difference of potential of 580 millivolts. What is the hydrogen-ion concentration and P_H value of the solution? What color would be given to the solution by a drop of methyl orange?

Ans. 8.1×10^{-6}; 5.09; yellow.

See Miscellaneous Problems for problems on electrometric titrations.

PART V

MISCELLANEOUS PROBLEMS

Significant Figures. Precision Measures. Chemical Balance

340. If in the analysis of a given substance a variation of 0.3 per cent is allowable, to how many milligrams should a 10-gram sample be weighed?

341. How many significant figures are in the value 16×10^3? In the value 16.00×10^3?

342. In the following multiplication the last figure in each of the three factors is uncertain. How many significant figures are contained in the product as given, and which digits should be rejected as superfluous?

$$2.0000 \times 0.30 \times 500 = 300.00$$

343. A temperature of 78.6°F. is read from a thermometer graduated to single degrees. A pressure of 762.3 millimeters of mercury is read from a barometer graduated to tenths of a millimeter. Convert the temperature to degrees of absolute temperature and multiply by the pressure in millimeters, retaining the correct number of significant figures in each term and in the product.

344. The percentage of carbon in a sample of steel is found to be 0.42 per cent. The calculations involve only multiplication and division. To how many decimal places would you weigh out a 1-gram sample in order to duplicate the result?

345. In running a test it was necessary to multiply grams per liter (129.3) by the number of liters (11.5), and to subtract from the product the value obtained by multiplying 1.973 grams per liter by 7.3 liters. The result as reported was 1,472.5471 grams. Which significant figures should be rejected? If each value of the data given may differ from the true value by one in the last place, what is the percentage error of the least precise term?

346. In standardizing a solution the values 1.090 and 1.097 are obtained for the normality. It is known that in titrations this solution is to be used in amounts of less than 10 c.c., the volumes being read from a burette to hundredths of a cubic centimeter, and the last figure estimated. In calculation, the normality is to be multiplied by the number of cubic centimeters. Is it necessary to attempt to obtain a closer check in the standardization of the solution?

347. In measuring the length of a certain object, three measurements were taken and the following values were obtained: 67.27, 67.23, and 67.20 feet. In converting the length to inches, how many figures should be retained in

the answer? If the length were known to be 67.250 feet what is the percentage deviation of each of the above values from the true value? In converting them all into inches, what would be the percentage deviation of the result in each case?

348. In calculating an analytical result, it is necessary to convert a weighed amount of silver chloride (1.37 grams) to metallic silver. This is done by multiplying the weight of the silver chloride by the atomic weight of silver (107.88) and dividing by the molecular weight of silver chloride (107.88 + 35.46). Express the required weight of silver to the correct number of significant figures.

349. The calculation of a certain analysis involves only multiplication and division. Directions call for a 5-gram sample, and the analyst knows that the proportion of the constituent sought is approximately (*a*) 1 per cent; (*b*) 10 per cent, of the total sample. How accurately must the sample be weighed in order that the analyst may be justified in expressing the result to two figures beyond the decimal point?

350. In the calculation of an analytical result, a value which has been found by two analyses to be 0.1129 and 0.1137 is to be multiplied by 2.36 c.c. as measured by an ordinary burette graduated to tenths of a cubic centimeter. Express the result to the proper number of significant figures.

351. A sample of limonite was analyzed by twelve students at different times during the college year. The values obtained for the percentage of iron were 34.62; 34.42; 34.60; 34.48; 33.71; 34.50; 34.50; 34.22; 34.41; 35.00; 34.65; 34.44. What is the mean value, the mean deviation of a single result, and the deviation of the mean?

352. A sample of material was sent to two chemists. Each used the same method and reported the results of 4 analyses, as follows:

Chemist A	Chemist B
30.15	30.251
30.15	30.007
30.14	30.101
30.16	30.241

Calculate in each case the mean value and its deviation measure. Other conditions being equal which is probably the better analyst?

353. What would be the weight of a piece of gold *in vacuo* if in air against brass weights it weighs 14.2963 grams?

354. *In vacuo*, a quartz dish weighs 22.9632 grams. Calculate the weight in air against brass weights.

355. In determining an atomic weight, a final product which has a specific gravity of 6.32 is weighed in air against gold weights. What percentage error would be made by failing to convert this weight (10.0583 grams) to the weight *in vacuo*?

356. Find to the nearest tenth of a milligram the weight *in vacuo* of a piece of silver which weighs 20.0113 grams in air against brass weights.

357. Find the weights *in vacuo* of two crucibles, one of gold and one of aluminum each weighing exactly 15 grams in air against brass weights. What would the gold crucible weigh in air against aluminum weights?

358. What is the specific gravity of a solid which weighs approximately 20 grams in air against brass weights and the weight of which increases by exactly 0.01 per cent *in vacuo?* What is the specific gravity of a similar substance the weight of which decreases by 0.01 per cent *in vacuo?*

359. Explain why the sensitivity of a chemical balance decreases with increasing load.

360. What are the relative advantages of a short-arm and a long-arm balance?

361. Using the weights given in the example cited in Sec. 10 a crucible is weighed in the ordinary way and balances with the rider on 4.7 milligrams and the following weights on the pan: 0.01; 0.01′; 0.02; 0.05; 5.0; 20.0. What is the weight of the crucible in terms of the 10-gram standard chosen? If in this case the 5-gram weight had been used as the final standard, what would have been the weight of the crucible?

362. Using the weights given in the example of Sec. 10 a dish is weighed in the ordinary way and balances with the rider on 8.4 milligrams and with the 20-, the 10′-, the 10-, and the 0.20-gram weights on the right-hand pan. What is the true weight of the dish in terms of the 10′-gram weight chosen? What is its weight using the 20-gram weight as the standard, and using the 5-gram weight as the standard?

363. If with a temporary 0.01-gram weight standard the 5-gram weight weighs 5.0028 grams, the 10-gram weight weighs 10.0054 grams, and the 50-gram weighs 50.0251 grams, calculate the correction to be applied to each weight if (*a*) the 5-gram weight, (*b*) the 10-gram weight, (*c*) the 50-gram weight is taken as the final standard.

Ionization Constants. Solubility Products

364. In a 0.2-molal solution of ammonium hydroxide what percentage of the base is un-ionized?

365. How much water must be added to 300 c.c. of a 0.2 molal solution of acetic acid so that its percentage ionization is doubled in value?

366. What is the concentration of hydroxide ion in a thousandth molal solution of silver hydroxide?

367. What are the approximate concentrations of $H_2PO_4^-$, HPO_4^-, and $PO_4^{\equiv}$ ions in a 0.1 molal solution of phosphoric acid? What are the concentrations of these ions if to the 0.1 molal solution is added sufficient hydrochloric acid to bring the hydrogen-ion concentration to 1 molal?

368. What are the approximate concentrations of HCO_3^- and CO_3^- in a 0.001 molal solution of carbonic acid?

369. Calculate the cyanide-ion concentration and the percentage ionization in a 0.03 molal solution of hydrocyanic acid.

370. Benzoic acid is a monobasic acid which is 2.4 per cent ionized in 0.1 molal solution. How many moles of sodium benzoate (completely

ionized) must be added to a liter of 0.05 molal benzoic acid solution in order to decrease its ionization at that concentration tenfold?

371. Calculate the hydrogen-ion concentration in a solution containing 25 c.c. of 4 N acetic acid in a total volume of 1,200 c.c. Calculate the hydrogen-ion concentration in the same solution after adding 15 grams of anhydrous sodium acetate which is 85 per cent ionized.

372. What is the percentage ionization of acetic acid in 0.15 N solution? What is the hydrogen-ion concentration in 500 c.c. of a solution which is 0.1 molal in $HC_2H_3O_2$ and contains 1 mole of sodium acetate (85 per cent ionized)?

373. What is the approximate sulphate-ion concentration and the approximate hydrogen-ion concentration in a 0.06 molal solution of H_2S? To what value must the hydrogen-ion concentration be brought in such a solution by means of a strong acid so that the sulphide-ion concentration is decreased a hundred thousand fold?

374. What is the solubility product of calcium oxalate if its solubility is 6.2×10^{-5} moles per liter?

375. Six milligrams of magnesium hydroxide will just dissolve in 500 c.c. of water. What is the solubility product of magnesium hydroxide?

376. Calculate the solubility product of lead phosphate from the fact that its saturated solution contains 1.05×10^{-5} gram of lead ions per 100 c.c.

377. The solubility products of Ag_2CrO_4 and $Ag_2Cr_2O_7$ are 1.7×10^{-12} and 2.7×10^{-11} respectively. How many milligrams of silver will be present in each case when excess of the salt is shaken with 250 c.c. of water?

378. If the solubility product of Bi_2S_3 is 2.6×10^{-91} find the weight of bismuth ions in grams which must be present in a liter of solution to cause precipitation of Bi_2S_3 in a solution which is 0.1 molal in H_2S and contains 0.01 mole of hydrogen ions per liter.

379. The solubility product of Ag_2SO_4 is 7.0×10^{-5}. Would this compound be suitable as a final precipitate in a gravimetric analysis? What would the concentration of sulphate ions theoretically have to be in a solution so that only 30 milligrams of silver would remain dissolved in 500 c.c. of the solution?

380. Which contains the more silver, a saturated solution of silver iodate (solubility product $= 2.3 \times 10^{-8}$) or of silver dichromate (solubility product $= 2.7 \times 10^{-11}$)?

381. What is the difference in the number of milligrams of lead contained in 300 c.c. of a saturated solution of lead phosphate (solubility product $= 1.5 \times 10^{-32}$) and the number of milligrams of lead contained in 300 c.c. of a saturated solution of lead chromate (solubility product $= 1.8 \times 10^{-14}$)?

382. Calculate the ionization constant of ammonium hydroxide from the fact that in 0.1 N solution it is 1.3 per cent ionized. In a 0.2 N solution what is the concentration of hydroxide ions and what is the percentage ionization? If to a 0.1 N solution of NH_4OH are added 3 moles of NH_4^+ ions per liter what would be the concentration of hydroxide ions and the percentage ionization of the NH_4OH? How many grams per

liter of magnesium could remain dissolved in one liter of the 0.1 N NH_4OH solution and how many grams of magnesium could theoretically remain dissolved in 1 liter of the above NH_4OH solution containing the excess NH_4^+ ions? Solubility product of $Mg(OH)_2 = 3.4 \times 10^{-11}$.

383. If 200 c.c. of a solution containing 0.5 c.c. of 6 N HCl (85 per cent ionized) are saturated with hydrogen sulphide how many grams of Fe^{++} can be present in the same solution? Solubility product of $FeS = 1.5 \times 10^{-19}$.

384. If H_2S is passed into a solution 0.1 molal in Cu^{++} and 0.1 molal in Bi^{+++}, which element will precipitate first? Solubility product $CuS = 8.5 \times 10^{-45}$; solubility product $Bi_2S_3 = 2.6 \times 10^{-91}$.

385. How many cubic centimeters of 12 N HCl must be present in 100 c.c. of a solution containing 0.0050 gram of $PbCl_2$ so that on saturating the solution with H_2S no lead will precipitate? Solubility product of $PbS = 4.2 \times 10^{-28}$. Assume HCl is completely ionized in this solution.

386. Five hundred c.c. of an acid solution of 1.15 grams of $ZnSO_4.7H_2O$ are saturated with hydrogen sulphide. The resulting solution is found to be 0.05 molal in H^+ ions. What fraction of the zinc has been precipitated? How much 12 N HCl should be added to 500 c.c. of a neutral solution containing 1.00 gram of $ZnSO_4.7H_2O$ so that no precipitate will be obtained on saturating with hydrogen sulphide? Solubility product of $ZnS = 1.2 \times 10^{-23}$. Assume HCl is completely ionized.

Chemical Factors. Atomic Weights

387. Calculate the chemical factors for (*a*) Sn in SnO_2; (*b*) MgO in $Mg_2P_2O_7$; (*c*) P_2O_5 in $Mg_2P_2O_7$; (*d*) NH_3 in $(NH_4)_2PtCl_6$; (*e*) Fe_3O_4 from Fe_2O_3.

388. Calculate the log factors for (*a*) Cr in $PbCrO_4$; (*b*) Cr_2O_3 from $PbCrO_4$; (*c*) KCl from Pt (obtained by igniting and washing K_2PtCl_6).

389. How many ounces of Mn_3O_4 could be obtained from 1 pound of MnO_2?

390. How many pounds of phosphorus are contained in 1 ton of $Ca_3(PO_4)_2$?

391. How many ounces of sulphur are in 1 pound of $BaSO_4$?

392. A manufacturer using potassium cyanide in a process involving its use as cyanide only, substituted sodium cyanide at 45 cts. a pound for a chemically equivalent quantity of potassium cyanide at $2 a pound. How much did he save per pound of KCN?

393. What weight of AgBr could be obtained from 4.7527 grams of $Ag_2Cr_2O_7$?

394. An ammonium salt is converted into $(NH_4)_2PtCl_6$ and the latter ignited until only the Pt remains in the crucible. If the residue weighs 0.1000 gram, what weight of NH_3 was present in the original salt?

395. What weight of water could be obtained by strongly igniting 2 grams of datolite ($CaB(OH)SiO_4$)?

396. A sample of pure dry $CaCO_3$ loses on ignition 0.6427 gram. Calculate the weight of CaO in the original sample.

397. What is the percentage of silver in $Ag_2Cr_2O_7$?

398. What are the percentages of the constituent oxides in a pure sample of titanite ($CaTiSiO_5$)?

399. What are the percentages of the constituent oxides of borax ($Na_2B_4O_7.10H_2O$)?

400. What are the percentages of Na_2O, H_2O, and SiO_2 in pectolite ($HNaCa_2(SiO_3)_3$)?

401. What are the percentages of PbO, CO_2, and water in "white lead" ($2PbCO_3.Pb(OH)_2$)?

402. Find the percentage composition in terms of the oxides of the following:

(*a*) $FeSO_4.7H_2O$.
(*b*) $K_2SO_4.Al_2(SO_4)_3.24H_2O$.
(*c*) $3Ca_3(PO_4)_2.CaCO_3$.

403. In the determination of the atomic weight of phosphorus, if the ratio $\frac{3Ag}{Ag_3PO_4}$ is found to be 0.77300 and the atomic weights of silver and oxygen are known to be 107.88 and 16.00000, respectively, how many significant figures may be retained in the atomic weight of phosphorus as determined? What is the value of this atomic weight?

404. In determining the atomic weight of aluminum, Richards and Krepelka prepared pure samples of $AlBr_3$ and experimentally determined the weight of silver required to precipitate the halogen. Results of four experiments were as follows:

	Wt. $AlBr_3$ (in Vacuo)	Wt. Ag (in Vacuo)
Sample 1	5.03798	6.11324
Sample 2	5.40576	6.55955
Sample 3	3.41815	4.14786
Sample 4	1.98012	2.40285

If the atomic weight of silver is 107.88 and that of bromine is 79.916 what is the mean value obtained for the atomic weight of aluminum?

405. The ratio of the weight of silicon tetrachloride to the weight of an equivalent amount of silver has been found to be 0.393802 ± 0.000008. Assuming Cl = 35.457 and Ag = 107.880, calculate the atomic weight of silicon.

406. Classen and Strauch have determined the weights of bismuth oxide obtainable from several samples of pure bismuth triphenyl. In one such determination, 5.34160 grams of $Bi(C_6H_5)_3$ gave 2.82761 grams of Bi_2O_3. Calculate the atomic weight of bismuth as shown from these figures. C = 12.001, H = 1.0077.

407. What is the atomic weight of copper if 1.0000 gram of Cu is obtained by the reduction of 1.2518 grams of CuO?

408. From the ratios $\frac{NaNO_3}{NaCl} = 1.45422$, $\frac{AgCl}{Ag} = 1.328668$, and $\frac{NaCl}{Ag} = 0.541854$, and assuming N = 14.008, calculate the atomic weights of silver, sodium, and chlorine.

Volume of Reagents

409. How many grams of silver chloride will be formed by the addition of an excess of silver nitrate to 10.00 c.c. of hydrochloric acid (specific gravity 1.160, containing 31.52 per cent HCl by weight)?

410. Sulphuric acid of specific gravity 1.800 is to be used to precipitate the barium as barium sulphate from 1.242 grams of pure $BaCl_2.2H_2O$. Calculate the volume of acid necessary for precipitation.

411. How many cubic centimeters of ammonia (specific gravity 0.940) will neutralize 40.00 c.c. of H_2SO_4 solution (specific gravity 1.240)?

412. How many cubic centimeters of ammonia (specific gravity 0.960 containing 9.91 per cent of NH_3 by weight) will be required to precipitate the aluminum as $Al(OH)_3$ from a solution containing 500 grams of alum ($KAl(SO_4)_2.12H_2O$) and 100 c.c. of HCl (specific gravity 1.12 containing 23.82 per cent HCl by weight)?

413. What volume of HNO_3 (specific gravity 1.050) is required to oxidize the iron in 1 gram of $FeSO_4.7H_2O$ in the presence of sulphuric acid? ($6FeSO_4 + 2HNO_3 + 3H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$.)

414. Alum, $KAl(SO_4)_2.12H_2O$, weighing 0.6000 gram is dissolved in water and 10.0 c.c. of hydrochloric acid (specific gravity 1.12 containing 23.82 per cent HCl by weight) are added. It takes 5.11 c.c. of ammonia (containing 28.33 per cent NH_3 by weight) to neutralize the acid and precipitate the aluminum as $Al(OH)_3$. Find the specific gravity of the ammonia, the normality of the acid, and the ratio of the base to the acid.

415. How many cubic centimeters of a solution of potassium dichromate containing 26.30 grams of $K_2Cr_2O_7$ per liter must be taken in order to yield 0.6033 gram of Cr_2O_3 after reduction, precipitation, and ignition of the chromium?

416. To a suspension of 0.310 gram of $Al(OH)_3$ in water are added 13.0 c.c of aqueous ammonia (specific gravity 0.900). How many cubic centimeters of sulphuric acid (specific gravity 1.18) must be added to the mixture in order to bring the aluminum into solution?

417. The arsenic in a 0.5-gram sample of As_2S_3 is oxidized to arsenic acid, and is precipitated with a solution of "magnesia mixture" ($MgCl_2.2NH_4Cl$). If exactly 12.6 c.c. of the mixture are required, how many grams of $MgCl_2$ per liter does the solution contain? ($H_3AsO_4 + MgCl_2 + 3NH_4OH \rightarrow MgNH_4AsO_4 + 2NH_4Cl + 3H_2O$.)

Indirect Gravimetric Analyses

418. A 1.0045-gram sample containing only $CaCO_3$ and $MgCO_3$ is strongly ignited. The weight of the ignited product (CaO and MgO) is 0.5184 gram. Calculate the percentage of Ca and of Mg in the original sample and in the ignited sample.

419. In duplicate analyses of a mixture of anhydrous sodium and potassium sulphates, the weights of barium sulphate obtained from 0.5000 gram of the mixture were 0.7713 and 0.7731 gram. Find the variation in percentage

of SO_4 in the mixture as thus determined, and also the variation in the percentage of anhydrous sodium sulphate in the mixture as calculated separately from each of the weights of barium sulphate obtained.

420. A mixture of BaO and CaO weighing 1.792 grams, when treated with sulphuric acid and transformed to mixed sulphates, weighs twice the original amount. What is the percentage of BaO in the mixture?

421. It is desired to mix $CaCO_3$ and $MgCO_3$ so that the ignited sample shall contain equal percentages of Mg and Ca. Calculate the percentages of the two components in the original mixture.

422. How many grams of $BaCO_3$ must be added to 2.40 grams of $MgCO_3$ so that the mixture will contain the same percentage of CO_2 as $CaCO_3$ does?

423. A mixture of NaBr, NaI, and $NaNO_3$ weighs 0.6500 gram. With silver nitrate, a precipitate of the halides of silver is obtained and is found to weigh 0.9390 gram. When heated in a current of chlorine gas the precipitate is converted entirely into AgCl weighing 0.6566 gram. What is the percentage composition of the original sample?

424. A precipitate of AgCl + AgBr weighs 0.8132 gram. On heating in a current of chlorine, the AgBr is converted into AgCl, the mixture losing 0.1450 gram in weight. What was the percentage of chlorine in the original precipitate?

425. A 1-gram sample consisting of a mixture of LiCl, KCl, NaCl, and NH_4Cl is dissolved in water and the solution is divided into two equal parts. One portion gives a precipitate with chloroplatinic acid which weighs 0.9500 gram and which loses 35 per cent of its weight on ignition. The other portion gives a precipitate with $AgNO_3$ weighing 1.2500 grams. What is the percentage of each constituent in the mixture?

426. A mixture of NH_4Cl and KCl weighs 0.5 gram. With chloroplatinic acid a precipitate is obtained which when ignited weighs 1.8400 grams. What is the percentage of NH_3 in the mixture? If the ignited precipitate were washed with water and reignited, what would be the weight obtained?

427. A mixture of AgCl and AgBr contains chlorine and bromine in the proportion by weight of Cl:Br = 1:2. What is the percentage of silver in the mixture? If one gram of the sample were heated in a current of chlorine, thereby converting the AgBr into AgCl, what would be the weight of the resulting mixture?

428. A sample of an impure mixture of NaCl, NaBr, and NaI weighing 1.5000 grams is dissolved in water and the solution is divided into two equal portions. One portion gives a precipitate of PdI_2 weighing 0.1103 gram. The other portion gives a precipitate of AgCl + AgBr + AgI weighing 1.2312 grams, and when these salts are heated in a current of chlorine they are all converted into AgCl weighing 1.0500 grams. What are the percentages of NaCl, NaBr, and NaI in the original sample?

429. A mixture of silver bromide and silver iodide weighs x grams. After heating in a current of chlorine the resulting silver chloride is found to weigh y grams. Derive an expression for the percentage of bromine and of iodine in the original mixture.

430. A mixture of silver chloride and silver iodide on being heated in a current of chlorine is converted entirely into silver chloride and is found to have lost exactly 6 per cent of its weight. What is the percentage of chlorine in the original mixture?

Electrolysis

431. On the basis of 30 per cent current yield, compute the cost of the power required to produce 1 pound of $NaMnO_4$ from a manganese anode and 0.3 N Na_2CO_3 solution. E.M.F. = 8 volts. Cost of current = 3 cts. per kilowatt-hour.

432. How many milligrams of silver can be deposited from solution in 23 minutes by a current of 0.7 ampere at 100 per cent efficiency? How long would it take the same current to deposit the same weight of nickel?

433. If a current of 0.25 ampere is passed through a copper sulphate solution and a 90 per cent current yield is obtained, compute (*a*) the weight of copper which can be deposited in one hour; (*b*) the gain in acidity in moles of sulphuric acid during that time.

434. If 6.3 amperes will deposit 0.532 gram of tin in 20 minutes from a solution of stannous salt, what is the current efficiency?

435. A pure alloy of copper and zinc is dissolved in acid and electrolyzed under 0.5 ampere (100 per cent efficiency). It is found that just 40 minutes are required to deposit all the copper. From the filtrate the zinc is precipitated and ignited to 0.245 gram of $Zn_2P_2O_7$. Calculate (*a*) grams of copper deposited; (*b*) per cent copper in the alloy; (*c*) volume of gas liberated; and (*d*) gain in acid normality of the solution assuming the volume to be kept constant at 500 c.c.

436. Assuming the volume of an electrolytic cell to be kept at 125 c.c., find the normal acid concentration of a solution containing 0.42 gram of copper, 0.20 gram of lead, and 0.26 gram of zinc as sulphates and 72 millimoles of sulphuric acid at the start (*a*) after just enough current has been passed to deposit all the lead as PbO_2 and assuming no other reaction takes place at the anode during that time; (*b*) after all the copper has deposited; and (*c*) when the current of 1.8 amperes has been continued 30 minutes longer. Compute the total volume of gas evolved during the entire electrolysis, measured under standard conditions.

437. Caustic potash is to be produced by the electrolysis of a solution of potassium chloride. Solution containing 100 grams of KOH per liter is required. An average current of 900 amperes is used and at the end of 5 hours, 102 liters of caustic potash, 1.520 N as an alkali, have been produced. How much longer must the electrolysis be continued in order to produce the desired concentration, and what is the current efficiency at the cathode?

438. What weight of $CuSO_4.5H_2O$ must be dissolved in water so that after complete deposition of the copper by electrolysis, a solution will be obtained which is equivalent to 100 c.c. of 0.1 N acid?

439. Pure crystals of $CuSO_4.5H_2O$ weighing 1.0000 gram are dissolved in water and the solution is electrolyzed with an average current of 1.3 amperes for 20 minutes. What weight of copper has been deposited? What volume of gas measured dry and under standard conditions has been liberated? If the resulting solution is made up to 100 c.c. with water, what is its normality as an acid?

440. Pure crystals of $CuSO_4.5H_2O$ are dissolved in water and the solution is electrolyzed with an average current of 0.60 ampere. The electrolysis is continued for 5 minutes after all the copper has been deposited and it is found that a total volume of 62.5 c.c. of gas measured dry at 18°C. and 745 mm. pressure has been evolved. What weight of crystals was taken for electrolysis? (Assume all the copper is deposited before hydrogen is evolved.) How many cubic centimeters of 0.1 N NaOH will the resulting solution neutralize?

441. A solution of brass in nitric acid contains 1.10 grams of copper, 0.50 gram of zinc and is exactly 2 N in acid. It is electrolyzed at 1.5 amperes and the volume is kept at 100 c.c. If all the current goes to the deposition of copper at the cathode what is the acid normality of the solution when all the copper has just deposited? What is the acid normality of the solution if the current is continued 20 minutes longer and 40 per cent of it goes to the reduction of nitrate ions to ammonium ions: (cathode) $NO_3^- + 8\epsilon + 10H^+ = NH_4^+ + 3H_2O$; (anode) $4H_2O - 8\epsilon = 8H^+ + 2O_2$. How long before the acid would be entirely destroyed?

442. Assuming 100 per cent current efficiency and assuming the electrolysis is discontinued as soon as the copper is deposited, compute the time required, the volume of gas evolved, and the gain in acidity in terms of millimoles of hydrogen ions when 0.8000 gram of brass in dilute HNO_3 is electrolyzed. Cathode gains 0.6365 gram and anode gains 0.024 gram. Current = 0.90 ampere. Compute also the percentage composition of the brass.

Elimination of a Constituent. Empirical Formulae

443. A manufacturer purchased 130 tons of material at 0.2 ct. per pound per cent A on a guarantee of 10 per cent A. The material was shipped in cars and on arrival the manufacturer had it analyzed. The chemist reported 10.46 per cent A, but neglected to state that he had dried the sample at 100°C. The manufacturer paid on a 10 per cent basis, figuring he had made money. In reality he lost $520. What was the percentage of moisture in the material?

444. A sample of crude copperas ($FeSO_4.7H_2O$) representing a large shipment was purchased at 1.25 cts. per pound. An analysis for iron content gave 20.21 per cent Fe. The shipment was stored for a considerable period during which time water of crystallization was lost. To fix the price at which the copperas was to be sold it was found that an increase of 0.023 ct. per pound would be necessary, due entirely to the change in the percentage of iron. Calculate the percentage of iron in the sample after storage. Attribute the increase to be due wholly to loss of water.

445. Ten tons of Na_2SO_3 containing 6.3 per cent moisture were purchased at the market price. During storage 10 per cent of the sodium sulphite was oxidized to sodium sulphate. The salt when sold contained 3.2 per cent of its weight of water. The salt was sold as C.P. Na_2SO_3 at the same price as purchased. Calculate the gain or loss in the transaction figuring the market price as 3.25 cts. per lb.

446. One pound of an ore lost half an ounce of water by drying at 110°C. to constant weight. The dried ore upon strong ignition with a flux lost 1.5 per cent of its weight of moisture and was also found to contain 20.10 per cent SiO_2. Find the per cent water and the per cent silica in the ore as received.

447. What weight of mineral containing ferrous iron should be taken for analysis so that twice the number of cubic centimeters of permanganate used for oxidation (20 c.c. = 30 c.c. of potassium tetroxalate solution which is 0.04 N as an acid) shall be three times the per cent FeO? Using this weight of sample, 15 c.c. of the permanganate are required and the water evolved by strong ignition weighs 0.0256 gram. What is the per cent FeO in a finely ground sample in which the percentage of water is 1.05?

448. A sample of welding compound was analyzed qualitatively and found to contain K^+, Cl^-, Na^+, F^-. A quantitative analysis gave 3.27 per cent F; 30.34 per cent K; 48.64 per cent Cl; and 17.75 per cent Na. What salts would you use and in what proportions would you mix them to duplicate the mixture?

449. A sample of Epsom Salts is supposedly C.P. $MgSO_4 \cdot 7H_2O$. On analysis of a sample weighing 0.8000 gram, the magnesium precipitated as $MgNH_4PO_4$ and ignited to $Mg_2P_2O_7$, was found to weigh 0.3900 gram.

The sulphate precipitated as $BaSO_4$, weighed 0.8179 gram.

(*a*) Is the sample chemically pure?

(*b*) If not, is the sample contaminated with excess magnesium salt or excess sulphate or excess water?

(*c*) Is the magnesium equivalent to the sulphate?

450. A sample of a certain hydrogen-potassium-magnesium-aluminum silicate weighing 1.2000 grams yields the following products: 0.0516 gram of water, 0.4000 gram of $KClO_4$, 0.9550 gram of $Mg_2P_2O_7$, and 0.1461 gram of alumina. What is the empirical formula of the mineral?

451. What is the empirical formula of a compound of the following composition?

Potassium	= 38.68 per cent
Hydrogen	= 0.50 per cent
Arsenic	= 37.08 per cent
Oxygen	= 23.74 per cent.

452. Zircon is a pure silicate of zirconium containing 33.0 per cent of silica. What is its empirical formula?

453. Analysis of an organic compound gives the following results:

Carbon	= 60.86 per cent
Hydrogen	= 4.38 per cent
Oxygen (by difference)	= 34.76 per cent
	100.00 per cent.

Calculate the empirical formula.

454. An organic acid is found to have a molecular weight of approximately 160 and to give the following analysis:

Carbon	=	57.82 per cent
Hydrogen	=	3.64 per cent
Oxygen (by difference)	=	38.54 per cent
		100.00 per cent.

Calculate the formula of the substance.

455. Calamine is a basic zinc silicate of the following composition:

ZnO =	67.5 per cent
H_2O =	7.5 per cent
SiO_2 =	25.0 per cent
	100.0 per cent.

Calculate its empirical formula.

456. What is the empirical formula of a mineral containing 3.37 per cent water, 19.10 per cent aluminum oxide, 21.00 per cent calcium oxide, and 56.53 per cent silica?

457. Calculate the empirical formula of the compound of the following composition:

Antimony =	49.55 per cent
Oxygen =	6.60 per cent
Chlorine =	43.85 per cent
	100.00 per cent.

458. A tungstate gives the following analysis:

WO_3 =	76.5 per cent
FeO =	9.5 per cent
MnO =	14.0 per cent
	100.0 per cent.

Calculate the empirical formula.

459. A silicate of the composition given below is found to have 85 per cent of its water in the form of water of crystallization. What is the empirical formula?

H_2O =	7.7 per cent
K_2O =	28.1 per cent
CaO =	20.4 per cent
SiO_2 =	43.8 per cent
	100.0 per cent.

460. From the following data obtained from the analysis of a feldspar, calculate the percentage composition of the sample and determine the empirical formula of the mineral, omitting the calcium from the formula and assuming the percentages of silica and alumina to be the most reliable.

Sample taken	= 1.2000 grams
Silica obtained	= 0.7751 gram
Alumina obtained	= 0.2255 gram
Calcium oxide obtained	= 0.0060 gram
KCl + NaCl obtained	= 0.3193 gram
K_2PtCl_6 obtained	= 0.7240 gram.

461. The qualitative analysis of a certain silicate shows the presence of a large quantity of calcium and only traces of other positive elements. In the quantitative analysis, the silica is removed and the calcium is precipitated from the filtrate as calcium oxalate. It is found that the number of cubic centimeters of 0.1660 N $KMnO_4$ required to oxidize the oxalate is almost exactly equal to the percentage of silica in the sample. What is the empirical formula of the pure mineral?

462. Heulandite is hydrous acid calcium metasilicate and yields on analysis 14.8 per cent water and 16.7 per cent alumina. If the calcium were precipitated as calcium oxalate from a 1-gram sample, 16.4 c.c. of N/10 $KMnO_4$ would be required for oxidation. Three-fifths of the water exists as water of crystallization. What is the empirical formula of heulandite?

463. Calculate the formula of a compound of carbon, hydrogen, nitrogen, and oxygen from the following data: Approximate molecular weight = 140. Decomposition of a 0.2-gram sample gives 34.87 c.c. of nitrogen when measured dry at 22°C. and 764 mm. pressure. The same weight of sample on combustion in oxygen yields 0.3824 gram of CO_2 and 0.0783 gram of H_2O.

464. A compound of C, N, and H yields a volume of nitrogen which when measured in cubic centimeters over water at 22°C. and 767 mm. pressure is equal to 155.5 times the number of grams of sample taken. The carbon and hydrogen are present in the molal ratio of 1:1. What is the empirical formula of the compound?

465. A 1-gram sample of a certain silicate yields 0.4525 gram of silica, 0.3840 gram of alumina, 0.6070 gram of K_2PtCl_6, and 81.9 c.c. of water vapor when measured at 120°C. and 750 mm. pressure. What is the empirical formula of the mineral?

466. Decomposition of a compound of carbon, hydrogen, nitrogen, oxygen, and bromine weighing 0.2000 gram yielded 8.70 c.c. of nitrogen (measured over water at 18°C. and 758 mm. pressure). Combustion in oxygen of the same weight of sample gave 0.1880 gram CO_2 and 0.01924 gram H_2O. After decomposition of 0.2000 gram with HNO_3, a precipitate of AgBr weighing 0.2674 gram was obtained. The molecular weight was found to be about 275. What is the formula of the compound?

467. Decomposition of 0.1500 gram of indol gave 16.42 c.c. of nitrogen when measured over water at 27°C. and 758 mm. pressure. Combustion

in oxygen of 0.2000 gram of the sample increased the weight of a potash bulb by 0.6026 gram, and of a calcium chloride tube by 0.2159 gram. Calculate the empirical formula of indol.

Calibration of Measuring Instruments

468. To calibrate a flask to contain a true liter at 20°C., how much water at 31°C., and 760 mm. pressure must be weighed into the flask in air against brass weights?

469. How much water must be weighed into a flask at 22°C., so that the flask may be marked to contain 500 c.c. according to the Mohr standard at 15°C?

470. A flask is marked to contain one true liter. Another flask is marked to contain one true liter according to the older standard of 15°C. Each flask is filled to the mark with water at 30°C. How many grams more water are contained in one flask than in the other?

471. A 5-gram sample of substance is dissolved in water, transferred to a flask which is marked to contain one true liter. In taking an aliquot portion for titration, a flask is used which has been marked to contain 500 c.c. according to the Mohr standard at 17.5°C. What percentage error would be introduced in the analysis? What percentage error would have been introduced if in taking the aliquot portion, a flask had been used which was marked to contain a true liter at the 15°C. normal temperature standard?

472. In calibrating a flask to contain one-half of a true liter using water at 30°C., what percentage error would be introduced by neglecting the expansion of glass in the calculation of the weight of water required?

473. What is the true volume of a flask that contains 398.70 grams of water at 26°C. when weighed in air against brass weights?

474. A pipette is marked to contain 100 c.c. according to the true liter standard. It is filled with water at 12°C. How much would the water weigh in air under normal barometric pressure against gold weights?

475. The inner diameter of the neck of a flask is 14 mm. and the flask contains 498.00 grams of water at 28°C. weighed in air against brass weights. How far above or below the meniscus of the water should a mark be placed in order to represent a volume of 500 c.c. according to the true liter standard?

476. A flask is marked to contain both a true liter and a Mohr liter at 15°C. It is filled to the lower mark with water at 17°C. To what temperature must the water be raised to reach the upper mark? Inner diameter of the neck of the flask = 15 mm.

477. A 50-c.c. burette is calibrated by weighing (against brass weights) the water delivered between 10-c.c. intervals in the graduations. Calculate from the following data the true volume of solution which the burette will deliver between each 10-c.c. interval, calculate the true total volume delivered between the 0-c.c. mark and the 50-c.c. mark and make a graph showing the correction which must be applied to the burette reading to obtain the true volume in any titration where the burette is initially filled to the zero mark. Temperature of the water = 26°C.

Graduation Intervals	Weight of Water Obtained
0.03 c.c.–10.07 c.c.	10.04 grams
10.07 c.c.–19.93 c.c.	9.84 grams
19.93 c.c.–29.97 c.c.	9.99 grams
29.97 c.c.–40.03 c.c.	9.97 grams
40.03 c.c.–49.96 c.c.	9.83 grams

General Acidimetry

478. Assuming complete neutralization in each case, what are the equivalent weights of the following substances when acting as acids and bases: (*a*) LiOH; (*b*) H_2SO_4; (*c*) Fe_2O_3; (*d*) $HC_2H_3O_2$; and (*e*) cream of tartar ($KHC_4H_4O_6$)?

479. How many grams of H_2SO_4 does a liter of 0.1 N sulphuric acid solution contain?

480. How many grams of hydrochloric acid gas does a liter of N HCl solution contain?

481. How many cubic centimeters of HCl (specific gravity 1.20 containing 39.11 per cent HCl by weight) are required to make a liter of 0.1 N solution?

482. How many grams of pure crystallized oxalic acid ($H_2C_2O_4.2H_2O$) must be dissolved and diluted to exactly one liter to make a 0.1 N solution for use as an acid?

483. How many grams of pure crystallized potassium tetroxalate ($KHC_2O_4.H_2C_2O_4.2H_2O$) must be dissolved in water and diluted to exactly 780 c.c. to make a 0.05 N solution for use as an acid?

484. How many cubic centimeters of sulphuric acid (specific gravity 1.200 containing 27.32 per cent H_2SO_4 by weight) are required to make one liter of 0.5 N solution?

485. Given: Standard sulphuric acid = 0.1072 N
Standard sodium hydroxide = 0.1096 N

How many cubic centimeters of sodium hydroxide solution are equivalent to 26.42 c.c. of the sulphuric acid solution?

486. Fifty cubic centimeters of 6 N ammonium hydroxide and 50 c.c. of 6 N hydrochloric acid are mixed. What is the approximate normality of the resulting ammonium chloride solution?

487. How many cubic centimeters of 0.3 N H_2SO_4 will be required to (*a*) neutralize 30 c.c. of 0.5 N KOH; (*b*) neutralize 30 c.c. of 0.5 N $Ba(OH)_2$; (*c*) neutralize 20 c.c. of a solution containing 10.02 grams of $KHCO_3$ per 100 c.c.; and (*d*) give a precipitate of $BaSO_4$ weighing 0.4320 gram?

488. What volumes of 0.5 N and 0.1 N HCl must be mixed to give two liters of 0.2 N acid?

489. How many cubic centimeters of water must be added to a liter of 0.1672 N sulphuric acid to make it exactly 0.1000 N?

490. What is the normality of a sulphuric acid solution which has a specific gravity of 1.839 and contains 95 per cent H_2SO_4 by weight?

491. Nitric acid, 15.8 N as an acid, has a specific gravity of 1.42. Calculate the per cent HNO_3 by weight.

492. Seventy-five cubic centimeters of hydrochloric acid (specific gravity 1.100 containing 20.01 per cent hydrochloric acid by weight) have been diluted to 900 c.c. What is the normality of the acid?

493. How could a solution of HCl be prepared of such normality that each cubic centimeter would represent 0.01 gram of $NaNO_2$ when the latter is determined by reducing to an ammonium salt, distilling with excess caustic alkali and titrating with the standard HCl?

494. A 0.2 N solution of barium hydroxide is to be prepared from pure $Ba(OH)_2.8H_2O$ crystals which have effloresced slightly. How may the solution be made if no standardized reagents are available?

495. Ten cubic centimeters NaOH $\simeq$ 0.0930 gram $H_2C_2O_4.2H_2O$

One cubic centimeter NaOH $\simeq$ 0.850 c.c. HCl.

What is the normality of the HCl solution?

496. What would be the normality of a solution of (*a*) HCl; and (*b*) H_2SO_4, if 40.0 c.c. of the acid are required to neutralize 0.500 gram of pearl ash containing 95 per cent total alkali calculated as K_2CO_3?

497. An acid solution is prepared by dissolving 19.264 grams of pure $KHC_2O_4.H_2C_2O_4.2H_2O$ in water and diluting to exactly 900 c.c. Fifty cubic centimeters of this solution are neutralized by 35.00 c.c. of KOH solution. What is the normal value of each solution?

498. One cubic centimeter NaOH $\simeq$ 1.012 c.c. HCl.

HCl is 0.4767 N.

One hundred cubic centimeters of the alkali have been diluted to 500 c.c. with the idea of preparing an exactly 0.1 N solution. How much too large is the volume?

499. One cubic centimeter NaOH $\simeq$ 0.0302 gram $H_2C_2O_4.2H_2O$.

One cubic centimeter HCl $\simeq$ 0.1123 gram $BaCO_3$.

What is the ratio by volume of HCl to NaOH? How much solid NaOH must be added to 800 c.c. of the alkali solution so that when the resulting solution is diluted to 1000 c.c. it will be 0.5 N? How much water must be be added to 1000 c.c. of the HCl to make it 0.5 N?

500. One cubic centimeter NaOH $\simeq$ 1.057 c.c. HCl.

The HCl is 0.4872 N.

To what volume must 100 c.c. of the alkali be diluted to make it exactly 0.5 N?

501. One cubic centimeter NaOH $\simeq$ 1.342 c.c. HCl.

One cubic centimeter HCl $\simeq$ 0.0225 gram $CaCO_3$.

How much water must be added to 1000 c.c. of the sodium hydroxide solution to make it 0.5 N? How much hydrochloric acid (specific gravity 1.190, containing 37.23 per cent HCl by weight), must be added to 1000 c.c. of the acid solution to make it 0.5 N?

502. How many cubic centimeters of ammonium hydroxide (specific gravity 0.900) will be required to neutralize 20.00 c.c. of nitric acid (specific gravity 1.420)? Calculate the normality of the ammonia solution as a base, the normality of the HNO_3 as an acid, and as an oxidizing agent assuming reduction to NO. Calculate the approximate normality of the ammonium nitrate solution formed.

503. In preparing an alkaline solution for use in volumetric work, a student, because of shortage of chemicals mixed exactly 46.32 grams of pure KOH and 27.64 grams of pure NaOH and after dissolving in water, diluted the solution to exactly one liter. How many cubic centimeters of 1.022 N HCl are necessary to neutralize 50.00 c.c. of the basic solution?

504. Pure dry sodium carbonate weighing 0.1042 gram is dissolved in 50.00 c.c. of 0.1024 N sulphuric acid and the solution heated to boiling to expel the carbon dioxide liberated by the reaction. The solution is then titrated with 0.1120 N sodium hydroxide. What volume of the base is necessary to neutralize the solution?

505. One gram of a mixture of 50 per cent sodium carbonate and 50 per cent potassium carbonate is dissolved in water and 17.36 c.c. of 1.075 N acid are added. Is the resulting solution acid or alkaline? How many cubic centimeters of 1.075 N acid or base will have to be added to make the solution exactly neutral?

506. From the following data, calculate the percentage purity of a sample of $KHSO_4$:

1 c.c. HCl $\simeq$ 1.206 c.c. NaOH
1 c.c. HCl $\simeq$ 0.02198 gram Na_2CO_3
Sample = 1.2118 grams
HCl used = 1.53 c.c.
NaOH used = 26.28 c.c.

507. A sample of Rochelle Salt ($KNaC_4H_4O_6.4H_2O$) after ignition in platinum to convert it to the double carbonate, is titrated with sulphuric acid using methyl orange as an indicator. From the following data calculate the percentage purity of the sample:

Weight of sample = 0.9500 gram
H_2SO_4 used = 43.65 c.c.
NaOH used = 1.72 c.c.
1 c.c. H_2SO_4 $\simeq$ 1.064 c.c. NaOH
NaOH = 0.1321 N.

508. A solution of hydrochloric acid of unknown strength is standardized against pure crystallized borax $Na_2B_4O_7.10H_2O$ using methyl orange as an indicator. From the following data, calculate the normality of the hydrochloric acid. Calculate the value of 1 c.c. of the sodium hydroxide solution in terms of pure crystallized borax.

Weight of borax = 0.5673 gram
HCl used = 47.26 c.c.
NaOH used = 1.20 c.c.
1 c.c. NaOH = 1.200 c.c. HCl.

509. In the standardization of an acid it was titrated against 1.000 gram of calcium carbonate (98.56 per cent pure). If 46.86 c.c. of HCl were added, the $CaCO_3$ dissolved, and the excess acid titrated with 5.21 c.c. of NaOH

solution of which 1 c.c. = 0.7896 c.c. HCl, calculate the weight of crude pearl ash to be taken for analysis so that each cubic centimeter of this HCl will represent 2 per cent K_2O.

510. One and five-tenths grams of crude K_2CO_3 are taken for analysis. What must be the strength of the HCl used in order that the burette reading shall indicate twice the percentage of K_2CO_3 in the sample?

511. A 500-c.c. graduated flask contains 150 c.c. of 0.2 N sulphuric acid. By adding more concentrated sulphuric acid the solution is brought up to the mark and after mixing is found to be exactly 0.3 N. What was the normality of the acid added? (Assume no change in volume due to chemical or heat effects.)

512. What would be the approximate normality of an acid solution made by mixing the following amounts of HCl solutions?

160 c.c. of 0.3050 N solution
300 c.c. of 0.4163 N solution
175 c.c. of 0.5020 N solution
250 c.c. of 0.2000 N solution.

513. What is the normality of an alkali solution made by mixing 50 c.c. of a solution containing 5 grams of NaOH with 50 c.c. of a solution containing 5 grams of KOH and diluting with water to 250 c.c.?

514. A sample of quicklime is to be analyzed for CaO and $CaCO_3$ by titrating with 0.1242 N HCl. It is desired to start with a 10-gram sample, mix with water, dilute and take aliquot portions of such size (*a*) that when titrated with HCl (using phenolphthalein as an indicator, in which case the $Ca(OH)_2$ only is neutralized) the number of cubic centimeters shall represent directly the percentage of CaO and (*b*) that when titrated by adding an excess of HCl, heating and titrating back with NaOH of the same normality as the HCl, the net number of cubic centimeters of HCl used shall represent directly the percentage of total calcium in terms of CaO. What portions should be taken?

515. A sample of soda ash is given to a student for analysis. He uses a 0.9000-gram sample and titrates with 0.3 N HCl, passing the end point and running back with exactly 8 c.c. of 0.3 N NaOH. His NaOH burette is accurately graduated, but the bore of the other burette, although uniform throughout its entire length, is not of correct size to agree with the graduations. Not knowing this, the student calculates the analysis and reports 64.50 per cent Na_2CO_3. If he had used the accurate burette for HCl and the other burette for NaOH, he would have reported 66.33 per cent. What was the true per cent Na_2CO_3 in the sample?

516. The "saponification number" of a fat or oil is defined as the number of milligrams of potassium hydroxide required to saponify one gram of the fat or oil. To a sample of butter weighing 2.010 grams are added 25.00 c.c. of 0.4900 N KOH solution. After saponification is complete, 8.13 c.c. of 0.5000 N HCl solution are found to be required to neutralize the excess alkali. What is the "saponification number" of the butter?

517. One gram of a sample of an ammonium salt is treated with an excess of strong sodium hydroxide and distilled. The distillate is absorbed in 50 c.c. of 1.072 N hydrochloric acid and the excess acid is titrated with 32.67 c.c. of 1.084 N sodium hydroxide solution. Calculate the percentage of NH_3 in the original sample.

518. A mixture of pure sodium carbonate and pure barium carbonate weighing 0.2000 gram requires 30.00 c.c. of 0.1N acid for complete neutralization. What is the percentage of each constituent in the mixture?

519. A sample supposed to be pure calcium carbonate is used to standardize a solution of HCl. The substance really was a mixture of $MgCO_3$ and $BaCO_3$ but the standardization was correct in spite of the erroneous assumption. Find the per cent MgO in the original powder.

520. A mixture of $BaCO_3$ and $CaCO_3$ weighs 0.5000 gram. The mixture is titrated with HCl, requiring 12.9 c.c. From the following data calculate the percentage of barium in the mixture:

$$30.4 \text{ c.c. HCl} \simeq 45.6 \text{ c.c. NaOH.}$$

1 c.c. of NaOH will neutralize that weight of $NaHC_2O_4$ which requires 6.67 c.c. of 0.1N $KMnO_4$ for its oxidation.

Indicators

521. Is pure water "acid," "neutral," or "basic" to phenolphthalein? Litmus? Methyl orange?

522. A solution which is red to congo red and to methyl red has approximately what hydroxide-ion concentration? How would it behave towards litmus and methyl orange?

523. How much water must be added to 10 c.c. of 0.00020 molal boric acid in order that the resulting solution shall be neutral to litmus?

524. How many grams of the following substances must be dissolved in 100 c.c. of water in order that the resulting solution shall react alkaline to phenolphthalein: (*a*) NH_3; (*b*) Na_2CO_3; (*c*) KNO_2; and (*d*) $NaHCO_3$?

525. How many grams of the following substances must be dissolved in 100 c.c. of water in order that the resulting solutions shall be acid to methyl red: (*a*) $H_2C_2O_4.2H_2O$; (*b*) H_2S; and (*c*) NH_4Cl?

526. If 2.7 grams of $NaC_2H_3O_2.3H_2O$ are dissolved in one liter of dilute $HC_2H_3O_2$ and the resulting solution gives an orange color with methyl orange, what is the approximate normality of the acetic acid?

527. Three hundred cubic centimeters of a solution containing NH_4OH is titrated with 48.50 c.c. of N/12 HCl. What should be the H^+-ion concentration at the end of the titration? What indicator is best suited for the titration?

528. What is the indicator constant of methyl red. This indicator changes to yellow when one-fifth of it is neutralized?

529. A solution is 0.1 molal with respect to phosphoric acid and 1 molal with respect to sodium phosphate. What color would be given by the addition of phenolphthalein? Methyl orange? Methyl red? Litmus?

530. In titrating a solution of a certain monoacidic base with NaOH, with methyl red as the indicator, the appearance of a shade of pink in the solution is taken as the end point. Assuming that the concentration of the resulting salt is 0.1 N and that the indicator used is best suited for this titration, what is the approximate ionization constant of the base?

531. If a 0.1 molal solution of H_3PO_4 is titrated with NaOH what should be the H^+ ion concentration when one H has been replaced by Na? When two H's have been replaced? If methyl orange is used in this titration, what fraction of the H_3PO_4 has been converted into NaH_2PO_4 at the color change? Into Na_2HPO_4? What fractions if phenolphthalein is used?

532. What is the percentage hydrolysis of KCN in 0.05 N solution at 25°C? If at a higher temperature it is 4 per cent hydrolyzed, what is the ion product of water at that temperature?

Double Indicator Titrations. Oleum Analysis

533. Calculate the grams of NaOH and the grams of Na_2CO_3 present in a mixture, which on analysis gives the following data: Sample = 4.000 grams. The sample is dissolved in water, the solution diluted to 250 c.c., and 25.00 c.c. are taken for analysis. An end-point with phenolphthalein in cold solution is obtained with 44.52 c.c. of N/5 HCl. A new portion of the same volume requires 46.53 c.c. of N/5 HCl for an end-point with methyl orange.

534. A mixture of soda ash and caustic soda weighs 0.7500 gram. Dissolved in water, phenolphthalein added, and titrated cold with half normal HCl, the color disappears when 21.00 c.c. have been added. Methyl orange is then added and the titration continued until the pink color appears. This requires 5.00 c.c. of acid in addition. Calculate the percentage of NaOH and of Na_2CO_3 in the sample.

535. A solution of alkali is prepared from NaOH contaminated with Na_2CO_3. Using phenolphthalein in the cold, 36.42 c.c. of the alkali are required to neutralize 50.00 c.c. of 0.5280 N H_2SO_4. Using methyl orange as the indicator, 35.60 c.c. of the alkali are required for the same amount of acid. How many grams of NaOH and of Na_2CO_3 are contained in each cubic centimeter of the alkali solution?

536. A mixture of sodium carbonate, sodium bicarbonate, and inert material weighs 1.0000 gram and with phenolphthalein requires 13.30 c.c. of N/2 acid to produce the color change in cold solution. With methyl orange, the same weight of sample requires 31.40 c.c. of the acid. What is the percentage of impurity in the sample?

537. A 1-gram sample containing a mixture of sodium carbonate, sodium bicarbonate and inert impurity is titrated with N/2 HCl. With phenolphthalein, a total of 10 c.c. is required; with methyl orange a total of 25 c.c. is required. Find the per cent Na_2CO_3 and the per cent $NaHCO_3$.

538. The qualitative analysis of a powder shows the presence of sodium, a carbonate and a little chloride. Titrated with methyl orange as an

indicator, 0.8000 gram of the powder reacts with 25.10 c.c. of half normal HCl and the same weight reacts with 18.45 c.c. of the acid with phenolphthalein in the cold solution. Compute the percentage composition of the original powder.

539. A substance reacts alkaline in aqueous solution, and the alkalinity is due to either Na_2CO_3 and NaOH, or to Na_2CO_3 and $NaHCO_3$. Compute the percentage of each alkaline constituent from the following data:

1.160 grams of powder react with 26.27 c.c. of 0.3333 N HCl when phenolphthalein is the indicator (in a cold solution) and with 59.17 c.c. when methyl orange is the indicator.

540. A solution containing 1 gram of sodium carbonate is titrated with N/2 HCl and a solution containing one gram of phosphoric acid is titrated with N/2 NaOH. With methyl orange as an indicator, how many cubic centimeters would be required in each case? With phenolphthalein as an indicator?

541. A mixture of Na_2HPO_4 and NaH_2PO_4 containing inactive impurity is analyzed with the following results: One and two-tenths grams of the powder react with 6.00 c.c. of N/2 HCl with methyl orange as the indicator. The same weight of powder reacts with 12.00 c.c. of N/2 NaOH when phenolphthalein is the indicator. Calculate the per cent NaH_2PO_4 and the per cent Na_2HPO_4 in the powder.

542. An oleum contains only H_2SO_4, SO_3, and SO_2. The H_2SO_4 and SO_3 are found to be present in equal parts by weight. When a sample of the oleum is titrated with NaOH (phenolphthalein as indicator) the volume of alkali required is found to be 50 times the volume of iodine of the same normality required to titrate the SO_2 in the same weight of sample. Calculate the percentage composition of the oleum.

543. A sample of fuming sulphuric acid contains only H_2SO_4, SO_2, and SO_3. A sample weighing 3.2030 grams is dissolved in water and requires 5.00 c.c. of 0.2N iodine solution to oxidize the SO_2. Another sample weighing 4.0301 grams is titrated with N/2 alkali with phenolphthalein as an indicator and requires 172.5 c.c. What is the percentage composition of the acid and what volume of alkali would have been used with methyl orange as the indicator?

544. The titration of a sample of fuming sulphuric acid containing no SO_2 shows the presence of an equivalent of 109.22 per cent H_2SO_4. Calculate the percentage composition of the sample and the percentage of combined SO_3.

545. A sample of oleum weighing 1.762 grams requires 42.80 c.c. of 0.8905 N NaOH for neutralization. Calculate the proportion by weight of free SO_3 to combined SO_3 in the sample.

546. A mixture of SO_3 and H_2SO_4 contains 91.18 per cent of total SO_3. Calculate the volume of half normal alkali required to titrate a solution of 1.030 grams of the mixture. What is the percentage of free SO_3 in the mixture? What is the equivalent of the mixture in terms of aqueous sulphuric acid containing 93.19 per cent H_2SO_4?

547. A mixture of pure acetic acid and acetic anhydride is dissolved in water and titrated with NaOH. The acidity of the sample expressed in terms of $HC_2H_3O_2$ is found to be 114 per cent. What is the composition of the original mixture? Acetic anhydride reacts with water to form acetic acid: $(CH_3CO)_2O + H_2O \rightarrow 2HC_2H_3O_2$.

General Oxidation Methods

548. Which is the more economical oxidizing agent, potassium nitrate at 65 cts. per pound or sodium nitrate at 50 cts. per pound?

549. A solution of nitric acid is 3 N as an acid. How many cubic centimeters of water must be added to 500 c.c. of the acid to make it 3 N as an oxidizing agent? Assume reduction of HNO_3 to NO.

550. How many cubic centimeters of 6 N HNO_3 would be necessary to dissolve 9.00 grams of copper? Assume reduction of HNO_3 to NO.

551. In the analysis of chrome iron ore, chromium is oxidized by fusion to chromate and determined by titration with ferrous ammonium sulphate. What is the equivalent weight in terms of (*a*) Cr_2O_3 and (*b*) Cr?

552. Titanium may be determined by reduction to $TiCl_3$ and subsequent oxidation to $TiCl_4$. What is the equivalent weight in terms of (*a*) TiO_2; (*b*) Ti and (*c*) $TiCl_4$?

553. Barium peroxide may be determined by adding water and acid to a sample of the solid and titrating the liberated hydrogen peroxide with permanganate. What is the equivalent weight in terms of (*a*) BaO_2; (*b*) H_2O_2 and (*c*) BaO?

554. How many cubic centimeters of N HCl will be required to dissolve 1 gram of iron out of contact with air, and how many cubic centimeters of N $K_2Cr_2O_7$ will be reduced by the resulting acidified solution?

555. One cubic centimeter of a thiosulphate solution is equivalent to 0.005642 gram of copper. Calculate the value of one cubic centimeter of the solution as a reducing agent in terms of (*a*) Sb; (*b*) As; (*c*) As_2S_3; and (*d*) Sb_2O_3.

556. $KHC_2O_4.H_2C_2O_4.2H_2O$ and $Na_2C_2O_4$ are to be mixed in the proper proportion so that the normality of a solution of the mixture as a reducing agent will be 2.15 times the normality as an acid. Calculate the proportion.

557. Calculate the normality as an acid and as a reducing agent of a solution made by dissolving a mixture of 20 grams of $H_2C_2O_4.2H_2O$, 10 grams of KHC_2O_4 and 15 grams of $KHC_2O_4.H_2C_2O_4.2H_2O$ in water and diluting to exactly 1,000 c.c.

558. What volume of HCl solution is required to dissolve 1 gram of pure iron out of contact with the air, if 3.00 c.c. of the acid will neutralize that volume of KOH solution which will react with 6.00 c.c. of a potassium acid oxalate solution which is 2 N as a reducing agent?

559. How much water must be added to 50 c.c. of a solution of nitric acid which is 2 N as an acid to make the resulting solution 2 N as an oxidizing agent? Assume reduction of the HNO_3 to NO.

560. Twenty-five cubic centimeters of HCl when standardized gravimetrically yield a precipitate of AgCl weighing 0.5465 gram. 24.36 cc. of the HCl exactly react with 27.22 c.c. of NaOH solution. 26.24 c.c. of the NaOH exactly react with 30.17 c.c. of $KHC_2O_4.H_2C_2O_4.2H_2O$ solution. How much water must be added to a liter of the oxalate solution to make it exactly 0.02500 N as a reducing agent?

561. A mixture of 20 c.c. nitric acid (12 N as an oxidizing agent) and 15 c.c. sulphuric acid (specific gravity 1.840) is diluted and partially neutralized by the addition of 25 grams of sodium hydroxide (95 per cent NaOH, 4 per cent Na_2CO_3, and 1 per cent H_2O) and finally completely neutralized by the addition of sodium hydroxide solution, 1 c.c. of which is equal to 1.074 c.c. of $KHC_2O_4.H_2C_2O_4.2H_2O$ which is N/10 as a reducing agent. Calculate the cubic centimeters of NaOH used.

562. A certain volume of a reagent will oxidize that amount of iron which will just dissolve in the same volume of 3 HCl. What is the normality of the oxidizing agent?

563. What is the normality of a nitric acid solution to be used as an oxidizing agent if it contains 55.79 per cent HNO_3 by weight and has a specific gravity of 1.350?

564. Molybdic oxide when reduced under certain conditions goes to a form represented by the formula $Mo_{24}O_{37}$. This oxide can be oxidized to MoO_3 by permanganate in acid solution. Calculate the volume of 0.1068 N $KMnO_4$ required to oxidize 1 gram of MoO_3 after reduction.

565. The hydrogen peroxide sold for medicinal purposes is often labelled "10 volume" which means that on ordinary decomposition it yields 10 times its volume of oxygen. What would be the normality of such a solution as an oxidizing agent? As a reducing agent?

Permanganate Process. Dichromate Process. Iodimetry

566. A student standardized a solution of KOH and one of $KMnO_4$ against the same salt ($KHC_2O_4.H_2C_2O_4.2H_2O$). The normality of the former was found to be 0.09963 as a base and of the latter to be 0.1328 as an oxidizing agent. By coincidence exactly 50 c.c. of solution were used in each standardization. Calculate the ratio of the weight of tetroxalate used in the first case to that used in the second case.

567. A powder is composed of oxalic acid ($H_2C_2O_4.2H_2O$), potassium binoxalate ($KHC_2O_4.H_2O$), and an inert impurity. Find the per cent of each constituent from the following:

One and two-tenths grams of the powder react with 37.80 c.c. of 0.2500 N NaOH solution; 0.4000 gram of powder reacts with 43.10 c.c. of 0.1250 N permanganate solution.

568. It requires 15.27 c.c. of $SnCl_2$ solution to reduce an amount of iron which can be oxidized by 16.27 c.c. of permanganate solution. This volume of the permanganate will also oxidize that amount of $KHC_2O_4.H_2C_2O_4.2H_2O$ solution which reacts with 16.24 c.c. of 0.1072 N NaOH. Calculate the normal value of the $SnCl_2$ solution.

569. A solution of ferrous sulphate is standardized against a solution of potassium permanganate which has been previously standardized against iron wire (99.85 per cent pure).

1 c.c. $KMnO_4$ = 0.005972 gram Fe.
1 c.c. $KMnO_4$ = 1.124 c.c. $FeSO_4$ solution.

Some time later the ferrous sulphate solution was standardized against a solution of potassium dichromate which had been standardized against similar iron wire.

1 c.c. $K_2Cr_2O_7$ = 0.005868 gram Fe.
1 c.c. $K_2Cr_2O_7$ = 1.122 c.c. $FeSO_4$ solution.

Assuming the normalities of $KMnO_4$ and $K_2Cr_2O_7$ solutions to be constant, calculate the percentage of Fe in the ferrous sulphate solution which had oxidized on standing.

570. From the following data compute the weight of iron ore to be taken for analysis such that the per cent Fe_2O_3 present is numerically equal to twice the number of cubic centimeters of $K_2Cr_2O_7$ used in the titration.

40 c.c. HCl solution = 2.880 grams of AgCl.

35 c.c. of HCl solution are equivalent to 40 c.c. of $KHC_2O_4.H_2C_2O_4$ solution

35 c.c. of tetroxalate solution are equivalent to 40 c.c. of $K_2Cr_2O_7$ solution.

571. A solution of dichromate is prepared by dissolving 4.883 grams of pure $K_2Cr_2O_7$ and diluting to exactly 1 liter; a solution of ferrous salt is prepared by dissolving 39.46 grams of $FeSO_4.(NH_4)_2SO_4.6H_2O$ and diluting to 1 liter. What volume of the dichromate solution must be transferred to the ferrous solution and thoroughly mixed so that the normality of one solution as a reducing agent shall be the same as the normality of the other solution as an oxidizing agent?

572. From the following data calculate the percentage of iron in a sample of limonite:

1 c.c. $K_2Cr_2O_7$ = 0.006299 gram Fe.
Dichromate solution used = 47.56 c.c.
Ferrous solution used = 2.85 c.c.
Sample taken for analysis = 0.6170 gram.
1 c.c. ferrous solution = 1.021 c.c. $K_2Cr_2O_7$.

573. Calculate the percentage of iron in a sample of crude ferric chloride weighing 1 gram if the iodine liberated by its action on an excess of potassium iodide is reduced by the addition of 50 c.c. of $Na_2S_2O_3$ solution and the excess thiosulphate is titrated with standard iodine, requiring 7.85 c.c.

45 c.c. iodine = 45.95 c.c. thiosulphate.
45 c.c. arsenite solution = 45.20 c.c. iodine.
1 c.c. arsenite solution = 0.00516 gram As_2O_3.

574. Pure $K_2Cr_2O_7$, weighing 0.3321 gram, was boiled with an excess of strong HCl. The evolved chlorine was passed into a solution of KI, and the I_2 liberated was titrated with 68.21 c.c. of $Na_2S_2O_3$ solution. Calculate the normality of the $Na_2S_2O_3$ solution.

575. In the analysis of sulphite liquor containing free sulphurous acid and calcium and magnesium sulphites, a sample weighing 1.028 grams requires 20.00 c.c. of NaOH solution for neutralization using phenolphthalein as an indicator. (30.00 c.c. of the NaOH will neutralize that weight of potassium acid oxalate which requires for oxidation 10.00 c.c. of permanganate containing 6.322 grams of $KMnO_4$ per liter.) At this point starch is added and the solution then requires 14.00 c.c. of iodine for a blue coloration. (1 c.c. of iodine is equivalent to 2 c.c. of a thiosulphate solution of which 4.00 c.c. will reduce the iodine liberated from KI by 1.00 c.c. of the above permanganate solution.) (*a*) Calculate the percentage of "free" SO_2 (*i.e.*, in the form of H_2SO_3). (*b*) Calculate the percentage of "combined" SO_2 (*i.e.*, in the form of calcium and magnesium salts). (*c*) Show by equations why the pink color produced at the first end-point disappears at the beginning of the second titration.

576. To 5 c.c. of a solution of a mixture of Na_2S and NaHS (specific gravity 1.032) is added a standard solution of HCl. The liberated H_2S is determined by adding excess iodine solution and titrating back with thiosulphate, and the resulting acidity is determined with NaOH. From the following data calculate the per cent Na_2S and the per cent NaHS in the sample:

1 c.c. HCl $\simeq$ 0.006005 gram $CaCO_3$
12 c.c. NaOH $\simeq$ 10 c.c. HCl
1 c.c. I_2 $\simeq$ 0.00601 gram Sb
10 c.c. $Na_2S_2O_3$ $\simeq$ 12 c.c. I_2
HCl used = 10.8 c.c.
NaOH used = 15.0 c.c.
I_2 used = 28.0 c.c.
$Na_2S_2O_3$ used = 15.0 c.c.

577. A solution which may contain Na_2S, NaHS, H_2S or mixtures of these is acidified and requires 20 c.c. of N/10 iodine solution for titration. The gain in acidity caused by the titration is equivalent to 10 c.c. of NaOH (1 c.c. $\simeq$ 0.006303 gram $H_2C_2O_4.2H_2O$). What does the solution contain? If 20 c.c. of iodine had been required and the gain in acidity had been represented by 17 c.c. of NaOH, what would the solution have contained?

578. A solution of a mixture of H_2S and NaHS is acidified with A c.c. of 0.1 N HCl and the total H_2S then present is determined by adding B c.c. of 0.1 N I_2 and titrating back with C c.c. of 0.1 N $Na_2S_2O_3$. The acidity at the end of the titration is measured by D c.c. of 0.1 N NaOH. Show that the number of grams of H_2S present in the original solution is given by the formula:

$$[C + 2D - (B + 2A)]\,0.001704$$

579. What weight of sulphite liquor should be taken for analysis so that the cubic centimeters of I_2 solution required (1 c.c. $\simeq$ 0.0125 gram $Na_2S_2O_3.5H_2O$) and the per cent total SO_2 shall be in the respective ratio of 20 to 3?

580. To 50 c.c. of a solution of chlorine in water an excess of potassium iodide was added; the liberated iodine was titrated with $Na_2S_2O_3$ using

starch as an indicator. From the data given calculate the volume of chlorine gas measured at 10°C. and 765 mm. pressure which is contained in 50 c.c. of the water solution.

$Na_2S_2O_3$ = 0.1246 N.
Volume required = 9.32 c.c.

Electromotive Series. Electrometric Titrations

581. When metallic iron is treated with hydrochloric acid it is oxidized to ferrous ions. What is the oxidizing constituent? What is it reduced to? Explain from the electromotive series why ferric ions are not formed as the oxidation product. Why are ferric ions formed when warm nitric acid is substituted for the hydrochloric acid?

582. Explain from the electromotive series the effect if any of passing bromine gas into (*a*) a solution of potassium iodide and (*b*) a solution of potassium chloride. Of adding (*a*) stannous chloride and (*b*) metallic tin, to an acid solution of antimony trichloride. Of electrolyzing an acid solution of nickel sulphate.

583. Which of the elements listed in the electromotive series show from their position in the series that they decompose or tend to decompose water at 25°C. (P_H value = 7)?

584. How many grams of copper can remain dissolved in solution which is 0.1 molal in aluminum ions and is in contact with metallic aluminum?

585. What is the E. M. F. of the cell Cd, Cd^{++} (1 molal)—Fe, Fe^{+++} (1 molal)?

586. What is the E. M. F. of the cell Zn, Zn^{++} (0.1 molal)—Ag, Ag^{+} (0.005 molal)?

587. What is the E. M. F. of the cell Ni, Ni^{++} (0.1 molal)—Fe, Fe^{+++} (0.0008 molal)?

588. What is the E. M. F. of the cell Cu, Cu^{++} (0.1 molal)—Cu, Cu^{++} (0.001 molal)?

589. A silver concentration cell with 0.1 N silver nitrate as one solution and a saturated silver chloride solution as the other solution gave an E. M. F. of 0.228 volt. Calculate the solubility of AgCl in water assuming the silver nitrate to be 80 per cent ionized and the silver chloride to be 100 per cent ionized.

590. A hydrogen concentration cell gives an E. M. F. of 0.116 volt. What is the ratio of the hydrogen-ion concentrations of the two solutions?

591. What is the P_H value of a solution of which the hydrogen-ion concentration is 10^{-6} N? 8.5×10^{-11} N? 0.1 N? What would be the E. M. F. shown by each solution using hydrogen-calomel electrodes?

592. The P_H value of a solution at room temperature is 9.3. What is its hydrogen-ion concentration? Its hydroxide-ion concentration? What E. M. F. would be given by this solution using hydrogen-calomel electrodes?

593. A hydrogen electrode and a calomel electrode in contact with a solution at 18°C. show a difference of potential of 740 millivolts. What is the P_H value of the solution? Is the solution "acidic" or "basic"? What

color would be given to the solution by a drop of phenolphthalein? Litmus? Methyl orange?

594. The electrometric titration of a 25-c.c. pipetteful of 0.2680 N H_2SO_4 with sodium hydroxide solution gave the following values of millivolts for the corresponding volumes of NaOH: 0.0 c.c. = 369.0 millivolts; 5.0 c.c. = 378.2; 10.0 c.c. = 388.1; 15.0 c.c. = 397.7; 20.0 c.c. = 405.8; 25.0 c.c. = 420.3; 28.0 c.c. = 460.1; 30.0 c.c. = 516.1; 30.5 c.c. = 690.4; 31.0 c.c. = 860.1; 35.0 c.c. = 949.4; 40.0 c.c. = 965.8; 45.0 c.c. = 982.2. Plot the millivolts of electrode potential as ordinates against the cubic centimeters of NaOH as abscissae and from the curve determine the P_H value at the end point and the normality of the NaOH solution.

595. Plot the following values of millivolts against cubic centimeters of 0.1 N NaOH in the electrometric titration of 2.500 grams of vinegar. Calculate the percentage of acetic acid in the vinegar. At what volume of NaOH is the solution neutral and at what volume does the true end point occur? What is the P_H value at the end point? 0.0 c.c. = 420 millivolts; 4.0 c.c. = 475; 8.0 c.c. = 540; 12.0 c.c. = 588; 16.0 c.c. = 620; 18.0 c.c. = 638; 19.0 c.c. = 650; 19.4 c.c. = 670; 19.8 c.c. = 790; 20.0 c.c. = 830; 20.2 c.c. = 856; 20.5 c.c. = 875; 21.0 c.c. = 900; 22.0 c.c. = 930; 24.0 c.c. = 948; 28.0 c.c. = 970; 32.0 c.c. = 985.

596. Plot values on graph paper showing the relationship between millivolts and P_H values when using hydrogen-calomel electrodes. Include the range between $P_H = 14$ and $P_H = -2$.

597. Make a plot for the electrometric titration of 40 c.c. of 0.2133 N H_3PO_4 diluted with water to 200 c.c. and titrated with 0.2 N NaOH at 25°C. Show the P_H value at which the saturation of the first and second hydrogen ions of H_3PO_4 occur. 0.0 c.c. = 300 millivolts; 5.0 c.c. = 315; 10.0 c.c. = 350; 13.0 c.c. = 385; 13.5 c.c. = 398; 13.8 c.c. = 405; 14.0 c.c. = 415; 14.2 c.c. = 450; 14.4 c.c. = 525; 14.8 c.c. = 555; 15.5 c.c. = 566; 17.0 c.c. = 580; 20.2 c.c. = 603; 25.0 c.c. = 640; 27.5 c.c. = 658; 28.5 c.c. = 675; 28.8 c.c. = 685; 29.0 c.c. = 740; 29.2 c.c. = 760; 29.5 c.c. = 795; 30.0 c.c. = 815; 31.0 c.c. = 835; 35.0 c.c. = 870; 40.0 c.c. = 890.

598. A cleaner is known to contain, in addition to inert material, either NaOH, Na_2CO_3, or mixtures of these. The electrometric titration of a 1.000-gram sample in 100 c.c. of water with 0.2651 N HCl gave the following P_H values: 0.0 c.c. = 11.70; 5.50 c.c. = 11.68; 10.0 c.c. = 11.66; 20.0 c.c. = 11.60; 30.0 c.c. = 11.44; 45.0 c.c. = 10.98; 55.0 c.c. = 9.75; 60.0 c.c. = 8.76; 62.0 c.c. = 7.66; 64.0 c.c. = 6.31; 66.0 c.c. = 5.70; 68.0 c.c. = 5.40; 70.0 c.c. = 5.05; 72.0 c.c. = 4.81; 73.0 c.c. = 4.10; 74.0 c.c. = 2.44; 76.0 c.c. = 1.94; 78.0 c.c. = 1.72; 85.0 c.c. = 1.41; 95.0 c.c. = 1.16. Interpret the curve, stating which constituents are present and their approximate percentages. What is the E. M. F. value of the original solution?

599. The electrometric titration of 250 c.c. of $KMnO_4$ with 0.1076 N ferrous ammonium sulphate gave the following values for millivolts against cubic centimeters: 0.0 c.c. = 720 millivolts; 5.0 c.c. = 745; 10.0 c.c. = 756; 15.0 c.c. = 762; 20.0 c.c. = 770; 21.0 c.c. = 771; 21.5 c.c. = 770; 22.0

c.c. = 768; 22.4 c.c. = 390; 23.0 c.c. = 350; 25.0 c.c. = off scale. Plot the titration curve and determine the normality of the $KMnO_4$.

600. The chromium in 5 grams of steel was oxidized to chromate and then titrated electrometrically with 0.1039 N ferrous sulphate solution. Plot the curve and compute the percentage of Cr from the following data showing volts times ten against cubic centimeters: 0.0 c.c. = 6.50; 5.0 c.c. = 7.90; 10.0 c.c. = 8.00; 15.0 c.c. = 8.10; 20.0 c.c. = 8.20; 25.0 c.c. = 8.40; 30.0 c.c. = 8.60; 35.0 c.c. = 8.78; 36.0 c.c. = 8.85; 37.0 c.c. = 8.87; 37.5 c.c. = 8.87; 38.0 c.c. = 8.85; 38.3 c.c. = 8.84; 38.4 c.c. = 5.03; 39.0 c.c. = 4.45; 40.0 c.c. = 4.15; 45.0 c.c. = 3.90.

601. Calculate the percentage purity of a sample of $FeSO_4.(NH_4)_2SO_4.6H_2O$ from the following electrometric titration values. Sample = 1.0450 grams. Titrating solution = 0.1064 N $KMnO_4$. Millivolts against cubic centimeters: 0.0 c.c. = 250 millivolts; 2.0 c.c. = 350; 4.0 c.c. = 366; 8.0 c.c. = 393; 16.0 c.c. = 429; 20.0 c.c. = 450; 23.0 c.c. = 483; 24.0 c.c. = 540; 24.5 c.c. = 720; 25.0 c.c. = 865; 26.0 c.c. = 900; 28.0 c.c. = 930; 35.0 c.c. = 950. Plot the curve.

Precipitation Methods

602. In the analysis of a sample of silicate weighing 0.8000 gram, a mixture of NaCl and KCl weighing 0.2400 gram was obtained. The chlorides were dissolved in water, 50 c.c. of 0.1N $AgNO_3$ added, and the excess of silver titrated with KCNS solution using ferric alum as an indicator. In the last titration 14.46 c.c. were used and the reagent was exactly 0.3 per cent stronger in normality than the $AgNO_3$ solution. Find the percentage of K_2O and of Na_2O in the silicate.

603. A mixture of KCN, KCNS and K_2SO_4 (the last assumed to have no effect on the titration) weighing 0.6000 gram reacts with 18.4 c.c. of $AgNO_3$ solution containing 5.35 grams $AgNO_3$ per liter, before a permanent precipitate is obtained. At this point 75.0 c.c. more of the silver solution are added and the excess titrated with 12.0 c.c. of N/15 KCNS. Find the percentage composition of the mixture.

604. A mixture of LiCl and $BaBr_2$ weighing 0.5000 gram is treated with 37.60 c.c. of N/5 silver nitrate and the excess of the latter titrated with 18.50 c.c. of N/9 thiocyanate solution. Find the per cent Ba in the mixture.

605. The Ni in a 0.9000-gram sample of millerite is converted to the ammonia complex, and to the solution are added 0.25 c.c. of $AgNO_3$ solution containing 20 grams $AgNO_3$ per liter, and 5.00 c.c. of a KI solution which serves as the indicator. By adding two-10-c.c. pipettefuls of KCN solution (13 grams KCN per liter) the turbidity due to the AgI is found to have disappeared but just reappears on adding exactly 1.50 c.c. more of the $AgNO_3$. Calculate the per cent Ni in the millerite.

606. A sample containing KCN weighs 1.000 gram and requires 24.00 c.c. of N/12 $AgNO_3$ solution to obtain a faint permanent turbidity. What is the percentage of KCN? If the sample also contained 10 per cent KCl, what volume of the $AgNO_3$ solution would be required to precipitate the KCN and KCl completely?

607. A sample of feldspar contains 7.58 per cent Na_2O and 9.93 per cent K_2O. What must be the normality of a silver nitrate solution if 22.71 c.c. precipitates the chloride ions from the combined chlorides in a sample weighing 0.1500 gram?

608. A mixture of pure chlorides of potassium, lithium, and sodium weighing 0.4800 gram is obtained from 1.600 grams of a silicate. The chloride in this mixture is equivalent to 80 c.c. of 0.111N silver nitrate solution, and the potassium was equivalent to 0.1052 gram of K_2PtCl_6. Compute the percentage of K_2O and of Li_2O in the silicate.

609. What weight of KCN is equivalent to 30 c.c. of $AgNO_3$ solution containing 15 grams per liter (*a*) by the Volhard method for cyanide and (*b*) by the Liebig method?

610. A certain weight of ferrous ammonium sulphate contaminated with silica and water requires a number of cubic centimeters of barium chloride solution (25 grams of $BaCl_2.2H_2O$ per liter) to precipitate the sulphur exactly equal to the percentage of iron in the sample. What is the weight of sample?

611. A solution is known to contain dissolved KCl, KCNS, and KCN. The solution is titrated to a faint turbidity by the Liebig method for cyanide with 25.00 c.c. of 0.0880 N $AgNO_3$ solution. A 100-c.c. pipetteful of the $AgNO_3$ is then added, the solution is filtered and the excess silver in the filtrate requires 50.4 c.c. of N/12 KCNS solution. The precipitate of the three silver salts is boiled with HNO_3 which decomposes the AgCN and AgCNS and leaves the AgCl which is filtered off. The filtrate requires 65.0 c.c. of the above KCNS solution for the silver. Calculate the number of milligrams of KCN, KCl, and KSCN in the original solution.

612. A mixture of KCNS, KCN, KCl weighing 0.687 gram reacts with 30 c.c. of 0.05 N $AgNO_3$ in the Liebig titration and with 150 c.c. more in the Volhard titration. Find the percentage composition of the original powder

613. A sample of impure KCN weighs 0.950 gram and requires 22 c.c. of N/11 $AgNO_3$ to obtain a turbidity in the Liebig titration. What is the percentage of KCN? If the sample contained also 0.102 gram of NaCl what additional volume of $AgNO_3$ would be required for complete precipitation?

Gas Analysis

614. If a gas measured dry at 27°C. and 758 mm. pressure occupies a volume of 500 c.c., calculate its volume if the temperature is increased to 87°C. and the pressure is kept constant.

615. If hydrogen gas when measured over water at 23°C. and 772 mm. pressure occupies 97.3 c.c., what would be the volume under standard conditions?

616. A gas occupies a volume of 222 c.c. over water at 12°C. and 751 mm. pressure. What volume would it occupy over water at 31°C. and 770 mm. pressure?

617. $BaCO_3$ and $MgCO_3$ are mixed in the proportions by weight of 2:1 Calculate the volume of 6 N HCl to decompose a 5-gram sample.

Calculate the volume of CO_2 gas formed when measured dry at 22.4°C. and 758 mm. pressure. What would the volume of the gas be if it were collected under the same conditions over water (saturated with CO_2)?

618. What weight of impure calcite ($CaCO_3$) should be taken for analysis so that the volume in cubic centimeters of CO_2 obtained by treating the sample with acid and measuring the CO_2 dry at 18°C. and 763 mm. pressure shall equal the percentage of CaO in the sample?

619. One hundred and thirty cubic centimeters of a mixture of methane, air, and hydrogen are conducted over gently ignited palladium asbestos, after which the volume of the gas is 105 c.c. Both measurements are made at 20°C. and 750 mm. pressure using a Hempel pipette filled with water. Compute the percentage (by volume) of hydrogen in the original gas mixture and the weight of H_2O which could be formed from it.

620. Twelve grams of pure carbon undergo combustion in 31.3 liters of pure oxygen. Calculate the percentage-by-volume composition of the mixture after combustion.

621. Assume air to contain 20.9 volumes O_2 and 79.1 volumes of nitrogen. One hundred volumes of air are mixed with 95 volumes of hydrogen and the mixture exploded. What is the composition of the gas remaining and the volumes of the various components after cooling to 20°C. and 760 mm. pressure?

622. What volumes of nitrogen and carbon dioxide, each measured dry at 20°C. and 755 mm. pressure could be obtained by the combustion of 0.2010 gram of urea $[CO(NH_2)_2]$?

623. What volume of nitrogen measured over water at 30°C. and 760 mm. pressure could be obtained from 0.1860 gram of tetra-ethyl-tetrazone $[(C_2H_5)_2{:}N.N{:}N.N{:}(C_2H_5)_2]$?

624. How many cubic feet of oxygen would be required to burn a sample of steel weighing 2 grams and containing 99.00 per cent Fe, 0.25 per cent Mn, 0.45 per cent C, 0.10 per cent Si, 0.05 per cent P, 0.03 per cent S, and 0.12 per cent Cu? Compute the volume at 60°F. and 14.7 pounds pressure.

625. If in the analysis of a 1-gram sample of a carbonate, 18.0 c.c. of CO_2 measured over water at 18°C. and 763 mm. pressure were obtained, find the per cent of carbon in the sample.

626. What weight of limestone should be taken for analysis so that the volume of CO_2 evolved when measured over water at 15°C. and 770 mm. pressure shall be $\frac{2}{3}$ the percentage of CO_2 in the sample?

627. Compute the volume of oxygen required to oxidize a sample of pure Fe weighing 0.9000 gram assuming that the product of combustion is composed of 60 per cent Fe_2O_3 and 40 per cent Fe_3O_4 and that the gas is measured dry at 21°C. and 756 mm. pressure.

Halides. Silver. Alkalies

628. If a sample of silver coin weighing 0.2500 gram gives a precipitate of AgCl weighing 0.2991 gram, what weight of AgI could have been obtained from the same weight of sample, and what is the percentage of silver in the coin?

629. What is the least amount of C.P.$AgNO_3$ which will precipitate the chlorine in 2 grams of a mixture of 25 per cent NaCl, 65 per cent KCl, and 10 per cent NH_4Cl?

630. If in the analysis of a silicate a mixture of pure NaCl and KCl weighing 0.2500 gram was obtained from a sample weighing 0.7500 gram, and this mixture of chlorides contained 50 per cent chlorine, compute the percentage of K_2O in the silicate. What weight of potassium perchlorate would have been obtained if the chlorides had been analyzed by the perchlorate method?

631. In the J. Lawrence Smith method for potassium using a 0.5-gram sample of mineral, the analyst fails to expel all the ammonium chloride from the NaCl + KCl. The insoluble precipitate with chloroplatinic acid weighs 0.08921 gram. On ignition the weight is changed to 0.05969 gram. What would be the weight if the ignited precipitate were washed with water and dried, and what is the percentage of K_2O in the mineral?

632. Ten cubic centimeters of ammonium hydroxide (specific gravity 0.96) are diluted to exactly 100 c.c. in a calibrated flask and 10 c.c. withdrawn in a pipette, made acid with hydrochloric acid, and an excess of chloroplatinic acid is added. After evaporation and dilution with alcohol, the insoluble residue is dried and found to weigh 1.240 grams. Calculate the percentage of NH_3 by weight in the original ammonia sample.

633. With a 0.5000-gram sample of pure $NaKCaSi_2O_6$ what would be the financial saving of the perchloric acid method over the chloroplatinic acid method with 3 N perchloric acid at $18 per liter and platinum at $6 per gram? Assume these reagents to be added in sufficient amount to react with both the sodium and potassium in the sample, and that 80 per cent of the platinum is recovered. Neglect all other costs.

Alkaline Earths. Limestone

634. What weight of limestone should be taken for analysis such that each milligram of the strongly ignited calcium oxalate precipitate corresponds to 0.1 per cent CaO in the sample?

635. What weight of dolomite should be taken for analysis such that the per cent CaO is the same as the number of cubic centimeters of 0.111N permanganate required to react with the calcium oxalate precipitate?

636. What weight of limestone should be taken for analysis such that the per cent Ca is 50 times the weight of the ignited calcium oxalate precipitate in grams?

637. A sample of $MgCO_3$ contaminated with SiO_2 weighs 0.5000 gram and loses 0.1002 gram on ignition. What volume of disodium phosphate solution (90 grams $Na_2HPO_4.12H_2O$ per liter) will be required to precipitate the magnesium as $MgNH_4PO_4$?

638. A sample of limestone contains only silica, ferrous carbonate, calcium carbonate, and magnesium carbonate. From a sample weighing 1.200 grams there were obtained 0.0400 gram of ignited ferric oxide, 0.500 gram of CO_2,

and 0.500 gram of magnesium pyrophosphate. Find the volume of 0.5 N ammonium oxalate solution required to precipitate the calcium as oxalate.

639. A limestone is found to contain 93.05 per cent $CaCO_3$ and 5.16 per cent $MgCO_3$. Calculate the weight of CaO obtainable from 3.00 tons of the limestone. What weight of $Mg_2P_2O_7$ could be obtained from a 3.000-gram sample?

640. A sample of dolomite is analyzed for Ca by precipitating as the oxalate and igniting the precipitate. The ignited product is assumed to be CaO and the analyst reports 29.50 per cent Ca in the sample. Owing to insufficient ignition, the product actually contains 8 per cent of its weight of $CaCO_3$. What is the correct percentage of Ca in the sample, and what is the percentage error?

641. A sample of magnesia limestone has the following composition:

Silica	= 3.00 per cent
Ferric oxide and alumina	= 0.20 per cent
Calcium oxide	= 33.10 per cent
Magnesium oxide	= 20.70 per cent
Carbon dioxide	= 43.00 per cent.

In manufacturing lime from the above, the carbon dioxide is reduced to 3.00 per cent. How many cubic centimeters of N $KMnO_4$ will be required to determine the calcium volumetrically in a 1-gram sample of the *lime?*

642. A sample of limestone containing 34.75 per cent Ca is given to a student for analysis. Using a 1-gram sample the student reports 35.26 per cent Ca. If the error was due to insufficient ignition of the calcium oxalate precipitate causing contamination of the CaO by $CaCO_3$, what was the percentage of $CaCO_3$ in the ignited product? What was the percentage error? What volume of sulphuric acid (specific gravity 1.06, containing 8.77 per cent H_2SO_4 by weight) should be added to this product to convert all the Ca into $CaSO_4$? What would be the new weight of the ignited product?

643. What weight of impure limestone should be taken for analysis so that the number of cubic centimeters of CO_2 evolved and measured over water at 15°C. and 770 mm. pressure shall be two-thirds the per cent of CO_2 in the sample?

644. From the following data compute the percentage of SiO_2, Al_2O_3, MgO, and CaO in a sample of cement weighing 0.6005 gram: Weight of SiO_2 = 0.138 gram. Weight of $Fe_2O_3 + Al_2O_3$ = 0.120 gram. Weight of $Mg_2P_2O_7$ = 0.0540 gram. Volume of N/7 $KMnO_4$ for the Fe in the above ignited precipitate = 2.05 c.c. Volume of this $KMnO_4$ required to titrate the precipitated calcium oxalate = 45.1 c.c.

645. A limestone contains only SiO_2, $CaCO_3$, $FeCO_3$, $MgCO_3$, $MnCO_3$. Calculate the percentage of CO_2 from the following data: Sample = 0.800 gram. $Fe_2O_3 + Mn_3O_4$ = 0.0521 gram and requires 5.00 c.c. of N/9 $KMnO_4$ for the iron. $CaSO_4$ = 0.725 gram. $Mg_2P_2O_7$ = 0.0221 gram.

Aluminum. Iron. Cobalt. Nickel

646. How many cubic centimeters of ammonium hydroxide (specific gravity 0.946 containing 13.88 per cent NH_3 by weight) are required to precipitate the iron as $Fe(OH)_3$ from a sample of pure $FeSO_4.(NH_4)_2SO_4.6H_2O$ which requires 0.34 c.c. of hot HNO_3 (specific gravity 1.350 containing 55.79 per cent HNO_3 by weight) for oxidation? Assume reduction of HNO_3 to NO.

647. One-tenth gram of an oxide of iron is fused with $KHSO_4$ and the fusion is dissolved in acid. The iron is reduced with stannous chloride, mercuric chloride is added, and the iron titrated with 0.1 N dichromate solution. If 12.94 c.c. were used, what is the formula of the oxide—FeO, Fe_2O_3 or Fe_3O_4?

648. A 1-gram sample of limonite containing inactive impurities is dissolved in acid, and the solution is divided into two equal portions. One portion is reduced and titrated with $KMnO_4$ (1 c.c. $\doteq$ 0.008193 gram $H_2C_2O_4.2H_2O$). The other portion is just neutralized, and 40 c.c. of 1.5N ammonia are added to precipitate the iron. This is in excess of the necessary amount, and the number of cubic centimeters in excess is equal to the number of cubic centimeters of $KMnO_4$ required in the volumetric process. What is the per cent Fe in the sample?

649. What weight of magnetite must be taken for analysis in order that after precipitating and igniting all the iron to Fe_2O_3 the percentage of Fe_3O_4 in the sample may be found by multiplying the weight in grams of the ignited precipitate by 100?

650. How many cubic centimeters of sulphurous acid containing 75.0 grams of SO_2 per liter are required to reduce the iron in 1 gram of ferric alum ($KFe(SO_4)_2.12H_2O$)? ($Fe_2(SO_4)_3 + SO_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4$.)

651. What weight of impure ferrous ammonium sulphate should be taken for analysis in order that one-third of the weight of the ignited Fe_2O_3 in milligrams may represent twice the percentage of FeO in the sample?

652. What is the percentage purity of a sample of ferrous sulphate $FeSO_4.7H_2O$ weighing 1 gram, if, after dissolving in water, adding 10 c.c. of 0.1 N hydrochloric acid, and oxidizing with bromine, 11.73 c.c. of N NH_4OH are required to precipitate the iron as $Fe(OH)_3$?

653. How many cubic centimeters of 0.1 N $KMnO_4$ are needed in the Zimmermann-Reinhardt method for iron, if by a gravimetric method 3.50 c.c. of 6 N ammonia water would be required to precipitate the iron after oxidation to the ferric condition?

654. A sample of ferrous ammonium sulphate is prepared for student analysis by intimately mixing pure crystals of $FeSO_4.(NH_4)_2SO_4.6H_2O$ with an inert substance. Using a 0.7650-gram sample a student correctly obtains 0.1263 gram of Fe_2O_3. What volume of barium chloride solution containing 25.0 grams of $BaCl_2.2H_2O$ per liter would be necessary to precipitate the sulphur from the filtrate? What is the percentage of inert material in the sample?

655. The Zimmermann-Reinhardt determination of total iron in 1.500 grams of mineral requires 27.30 c.c. of permanganate of which 1 c.c. = 0.01600 gram of hydrated potassium tetroxalate. Titration of ferrous iron alone by Cooke's method, requires the use of 22.00 c.c. of 0.1 N permanganate for the same weight of sample. If the latter method gives results which are 2 per cent too low (*i.e.*, 2 per cent of the correct value), what is the percentage of ferric iron in the sample?

656. A sample of ore weighing 0.8900 gram yields by electrolysis 0.2670 gram of Ni and Co and from the deposited metal a precipitate weighing 0.9405 gram is obtained with dimethyl glyoxime. Find the percentages of Ni and Co in the ore.

657. A nickel ore was analyzed by the volumetric method. The nickel solution was treated with KI solution and exactly 0.50 c.c. of $AgNO_3$ solution containing 0.0125 gram of $AgNO_3$ per cubic centimeter. The solution then reacted with 48.00 c.c. of KCN solution containing 0.0140 gram of KCN per cubic centimeter. What was the per cent Ni in the ore if the sample taken weighed 0.900 gram?

658. What weight of dried glyoxime precipitate would be obtained from 5 grams of steel containing 1.48 per cent Ni?

659. Calculate the per cent Ni in a sample of millerite from the following data: Weight of sample = 0.300 gram. Volume of KCN (31.2 grams per liter) = 10.00 c.c. Volume of $AgNO_3$ (25.5 grams per liter) = 1.40 c.c.

660. Compute the per cent Ni in a steel from the following data: Weight of steel = 1.50 grams. To the properly prepared solution were added 5 c.c. KI, 0.65 c.c. $AgNO_3$ (0.0125 gram per cubic centimeter), and 12.00 c.c. of KCN solution (0.0140 gram per cubic centimeter) were required.

Copper. Zinc. Lead. Tin. Non-ferrous Alloys

661. How many cubic centimeters of HNO_3 (specific gravity 1.130 containing 21.77 per cent HNO_3 by weight) are required to dissolve 5.00 grams of brass containing 0.61 per cent Pb, 24.39 per cent Zn, and 75.00 per cent Cu? Assume reduction of the HNO_3 to NO by each constituent. What fraction of this volume of acid is used for oxidation?

662. A solution of $(NH_4)_2HPO_4$ is made up to be 2 N as an ammonium salt. Calculate approximately the volume necessary to precipitate the zinc as $ZnNH_4PO_4$ in a sample of brass (90 per cent Cu, 10 per cent Zn) weighing 5.000 grams.

663. What volume of sulphuric acid (specific gravity 1.420) is required to displace the nitrate radical from the mixture of salts obtained by dissolving 25.00 grams of brass (68.29 per cent Cu; 31.50 per cent Zn; 0.21 per cent Pb) in nitric acid and evaporating to dryness?

664. Find the percentage of Pb_3O_4 in a sample of red lead which has been adulterated with PbO. Two and five-tenths grams of the pigment analyzed by the method of Lux are treated with 50 c.c. of potassium tetroxalate solution which is 0.1500 N as an acid, and the excess of the latter requires 30.00 c.c. of permanganate of which each cubic centimeter is equivalent to 0.005584 gram of iron.

665. If in the analysis of a brass containing 28 per cent Zn an error is made in weighing a 2.5-gram portion by which 0.001 gram too much is weighed out, what percentage error in the zinc determination would be made? What volume of a solution of di-ammonium phosphate, containing 90 grams of $(NH_4)_2HPO_4$ per liter, would be required to precipitate the zinc as $ZnNH_4PO_4$ and what weight of precipitate would be obtained?

666. A 5.300-gram sample of brass is dissolved in nitric acid, sulphuric acid is added and the whole evaporated until fumes are evolved. The lead sulphate obtained after filtration and ignition weighs 0.0299 gram. Calculate the percentage of lead in the brass.

667. What is the percentage of copper in a steel if with a 5-gram sample the volume of H_2S gas (measured under standard conditions) required to precipitate the copper as CuS is exactly 2 c.c. more than the volume of N/10 $Na_2S_2O_3$ solution subsequently required for the copper by the Low method?

668. A volume of 2.62 c.c. of HNO_3 (specific gravity 1.42) is required to dissolve a sample of brass containing 69.27 per cent Cu; 0.05 per cent Pb; 0.07 per cent Fe, and 30.61 per cent Zn. NO is liberated.

What was the weight of the brass? How many cubic centimeters of the HNO_3 were used as an oxidizing agent?

669. In the electrolysis of a sample of brass weighing 0.8000 gram, there are obtained 0.0030 gram of PbO_2, and a deposit of copper exactly equal in weight to the ignited precipitate of $Zn_2P_2O_7$ subsequently obtained from the solution. What is the percentage composition of the brass?

670. A solution of 0.8000 gram of $ZnSO_4.7H_2O$ in water containing 2 c.c. of 6 N HNO_3 is electrolyzed and the volume of the solution is kept constant at 100 c.c. Using a current of 1.2 amperes and assuming that 25 per cent of the current goes to the reduction of HNO_3 to N_2, how long before the zinc will start to deposit? What volumes of N_2 and of O_2 (at 60°F. and 76 cm. pressure) will be evolved during that time?

671. A sample of red lead is analyzed indirectly by means of N/5 $KMnO_4$ after reduction of the PbO_2 by 50.00 c.c. of N/5 $H_2C_2O_4$ solution. If t c.c. of $KMnO_4$ are used and the sample weighed a grams, derive an expression showing the method of calculating the per cent Pb_3O_4 in the sample. Assume red lead to be $2PbO.PbO_2$ ($PbO_2 + H_2C_2O_4 \rightarrow PbO + H_2O + 2CO_2$).

672. If 0.800 gram of a lead ore yields a precipitate of chromate which contains chromium sufficient to yield on treatment with an excess of KI in acid solution an amount of iodine to react with 48.0 c.c. of N/10 thiosulphate solution, find the per cent Pb in the ore.

673. What weight of zinc ore should be taken for analysis such that the number of cubic centimeters of 0.1 molal ferrocyanide solution used will equal the per cent Zn in the ore?

674. If a copper ore on being analyzed yields 0.235 gram of Cu_2S after heating with sulphur in a stream of hydrogen, how many grams of KIO_3 would react in the iodate method with the same weight of ore?

675. If 0.5000 gram of a copper alloy containing 25 per cent Cu requires 20.00 c.c. of KCN for titration what is the equivalent of 1 c.c. of the KCN (*a*) in terms of Ag (using KI as indicator) and (*b*) in terms of Ni. How many cubic centimeters of KIO_3 solution would have been required by the method of Jamieson, Levy and Wells if with an excess of KI, 15.00 c.c. of the KIO_3 would have liberated I_2 enough to react with a volume of N/10 thiosulphate equivalent to 0.100 gram of $K_2Cr_2O_7$?

676. A brass weighing 0.800 gram contains 75 per cent Cu, 23 per cent Zn, and 2 per cent Pb. What volume of N/10 $Na_2S_2O_3$ would be used in the determination of copper by adding KI and titrating the liberated iodine? What volume of N/20 $KMnO_4$ would be required for the lead if precipitated as chromate, dissolved, reduced with 25 c.c. of N/25 $FeSO_4$ and the excess ferrous ions titrated with the $KMnO_4$? What weight of zinc pyrophosphate would be obtained in the determination of zinc?

Nitrogen. Phosphorus. Vanadium. Arsenic. Antimony

677. Nitrogen, existing as nitride in a crucible steel, is determined by decomposing a 5-gram sample with HCl. The resulting NH_4Cl is decomposed with NaOH, and the liberated NH_3 is absorbed in 10.05 c.c. of H_2SO_4 which is exactly 0.009903 N as an acid. After absorption, the concentration of the H_2SO_4 is determined by adding an excess of KI and of KIO_3 and by titrating with standard $Na_2S_2O_3$ the I_2 liberated according to the reaction:

$$5KI + KIO_3 + 3H_2SO_4 \rightarrow 3K_2SO_4 + 3H_2O + 3I_2.$$

The $Na_2S_2O_3$ is of such strength that 42.08 c.c. are equivalent to the I_2 liberated from an excess of KI by 20.03 c.c. of 0.02584 N $KMnO_4$, and in the above titration 5.14 c.c. are used. Calculate the percentage of nitrogen in the steel.

678. A sample of impure ammonium chloride is dissolved in water and the solution is divided into two equal portions. One portion is made alkaline with NaOH and the liberated ammonia is distilled into 100 c.c. of 0.1N sulphuric acid which is then found to require 43.9 c.c. of 0.1320 N NaOH for neutralization. The other portion is treated with sodium hypobromite solution ($2NH_3 + 3NaOBr \rightarrow 3H_2O + 3NaBr + N_2$) and the liberated nitrogen is found to occupy 51.3 c.c. when measured over water at 20°C. and 753 mm. pressure. If the first method gives correct results, what is the percentage error of the gas-volumetric method?

679. How many cubic centimeters of magnesia mixture (1 N with respect to $MgCl_2$) will be required to precipitate the phosphorus from 0.2000 gram of pure apatite. Assume the formula of the latter to be $Ca_3(PO_4)_2.CaCl_2$?

680. Estimate the weight of $(NH_4)_3PO_4.12MoO_3$ obtainable from 0.2000 gram of pure apatite assuming the formula of apatite to be $Ca_3(PO_4)_2CaFCl$.

681. Calculate the per cent phosphorus in a steel from the following data:

Two grams of steel furnished a yellow precipitate which was dissolved in 20.00 c.c. of 0.5 N sodium hydroxide solution and the excess of the latter reacted with 27.00 c.c. of 0.333 N nitric acid.

682. A solution containing phosphoric acid was treated with ammonium molybdate and an abnormal yellow precipitate was obtained, which after drying may be assumed to have consisted of $[(NH_4)_3PO_4]_x[MoO_3]_y$. This precipitate was dried, weighed, dissolved in ammonia water, and the solution was made up to 500 c.c. Of this, 50 c.c. were taken, made acid with H_2SO_4, reduced with amalgamated Zn, and passed directly into an excess of ferric alum which served to oxidize the trivalent molybdenum back to the hexavalent condition. To oxidize the iron reduced by the molybdenum required a number of cubic centimeters of N/8 $KMnO_4$ equal to 15.39 times the weight in grams of the original yellow precipitate. What values of x and y may be taken in the formula of the yellow precipitate?

683. Phosphate reacts with ammonium molybdate to precipitate $(NH_4)_3PO_4.12MoO_3$. The precipitate may be dissolved, the molybdenum reduced to the valence corresponding to the oxide $Mo_{24}O_{37}$ and the reduced solution run into $Fe_2(SO_4)_3$ solution, which reoxidizes the molybdenum, reducing an equivalent amount of ferric iron to ferrous iron. The ferrous iron may then be oxidized by a measured volume of standard $KMnO_4$. Calculate the weight of a sample of steel to be taken for analysis so that every 100 c.c. of 0.1 N $KMnO_4$ used in the titration shall represent directly the per cent P.

Calculate in this process the equivalent weight of (*a*) P; (*b*) P_2O_5; (*c*) Mo; (*d*) MoO_3; and (*e*) $Mo_{24}O_{37}$.

684. A sample is prepared for student analysis by mixing pure apatite $(Ca_3(PO_4)_2.CaCl_2)$ with an inert material. If 1 gram of the sample gives 0.4013 gram of $Mg_2P_2O_7$, how many cubic centimeters of ammonium oxalate solution (40 grams of $(NH_4)_2C_2O_4.H_2O$ per liter) would be required to precipitate the calcium from the same weight of sample?

685. Calculate the per cent phosphorus in a sample of steel from the following data: 2.00 grams of steel furnished a normal yellow precipitate which when dissolved and treated with Zn reacted with 7.00 c.c. of 0.0833 N $KMnO_4$.

686. In the analysis of a sample of steel weighing 1.881 grams the phosphorus was precipitated with ammonium molybdate and the yellow precipitate was dissolved, reduced, and titrated with permanganate. If the sample contained 0.025 per cent P and 6.01 c.c. of $KMnO_4$ were used, to what oxide was the molybdenum reduced? One cubic centimeter of $KMnO_4$ was equivalent to 0.007188 gram of sodium oxalate.

687. What weight of steel should be taken for analysis such that the cubic centimeters of 0.111N caustic soda required to titrate a normal precipitate of ammonium phosphomolybdate will be 400 times as large as the per cent P in the steel?

688. A normal yellow precipitate of ammonium phospho-molybdate from a sample of bronze weighing 1 gram is reduced with zinc. The reduced solution requires 21.13 c.c. of 0.1 N permanganate to oxidize the molybdenum to the hexavalent condition. If the alloy contains exactly 0.2 per cent of phosphorus to what oxide was the molybdenum apparently reduced by the zinc?

689. What weight of steel should be taken for analysis such that the cubic centimeters of 0.125 N permanganate required to react with the reduced molybdenum (Blair Method) will be 200 times the per cent P in the steel?

690. Using a 2-gram sample of steel containing 0.007 per cent phosphorus, show by equations what reduction of the molybdenum was assumed from the following data:

Normality of $KMnO_4$ = 0.06193.
$KMnO_4$ = 2.71 c.c.

691. Assuming that vanadium like nitrogen forms 5 oxides and that any other oxide is a mixture of two or more of these, compute the apparent valence of the vanadium in the reduced condition and show what combination of oxides could give this. Use the following data: 0.08500 gram of $Na_2V_4O_9$ after an abnormal reduction was oxidized to the quinquivalent condition by 43.14 c.c. of $KMnO_4$ of which 40 c.c. reacted with 30 c.c. of potassium tetroxalate solution which was 0.08000 N as an acid.

692. A sample of stibnite weighs 0.5000 gram. The percentage of Sb as found by titration with 0.1 N iodine was 30.00 per cent. If the burette reading as recorded was 0.45 c.c. too large, what was the true percentage and what was the percentage error?

693. If the arsenic trichloride from 50 grams of impure copper is distilled off, absorbed in dilute alkali, and finally oxidized by 20 c.c. of N/50 iodine solution, find the per cent of arsenic in the sample.

694. A sample weighing 0.25 gram and containing arsenic is dissolved and the solution containing the trivalent element is electrolyzed (method of Hefti). Arsine is liberated and is conducted into 50 c.c. of N/8 iodine solution. The excess of the latter reacts with 20 c.c. of $Na_2S_2O_3$ solution of which 1 c.c. = 0.0050 gram of copper. Find (*a*) per cent of As_2O_3 in the sample and (*b*) the time required for electrolysis if a current of 3 amperes is used and only 40 per cent of the current is used in reducing the arsenic.

695. If 0.394 gram of $Na_2V_4O_9$ is reduced and requires 10.00 c.c. of permanganate (1 c.c. = 0.0536 gram $Na_2C_2O_4$) to oxidize the vanadium back to vanadic acid, find the valence of the reduced vanadium.

696. A nitrogenous substance weighing 6.05 grams furnishes enough NH_3 by the Kjeldahl method to react with 40.05 c.c. of 0.1 N H_2SO_4. What is the per cent of nitrogen?

697. The nitrogen is a 0.5-gram sample of urea, $CO(NH_2)_2$, is determined by the Kjeldahl method. The evolved ammonia is passed into 150 c.c. of 0.12 N H_2SO_4. How many c.c. of NaOH solution would be required for the excess acid if 1 c.c. NaOH = 0.00700 gram of hydrated oxalic acid?

698. The nitrogen in 5 grams of leather is converted into ammonium bisulphate. After treating with excess NaOH the NH_3 evolved is passed into 90 c.c. of 0.5 N acid and the excess acid titrated with 22.05 c.c. of 0.1 N NaOH. Find the percentage of nitrogen in the leather.

Hydrogen. Oxygen. Sulphur

699. What volume of water vapor could be obtained by strongly igniting 1.603 grams of $KHCaMgAl_2Si_4O_{14}.5H_2O$ if the gas is measured at 120°C. and 765 mm. pressure?

700. A sample of pure FeS_2 is analyzed by fusing a 2-gram sample and precipitating the sulphur as $BaSO_4$. How large an error in the weight of the precipitate must be made to produce an error amounting to 0.1 per cent of the apparent amount of S in the mineral?

701. A soluble sulphate weighing 0.9261 gram is analyzed. The precipitate of $BaSO_4$ on ignition is found to be 1.3724 grams. On further ignition the weight increases to 1.3903 grams due to the fact that the precipitate as first weighed had been partly reduced to BaS which on further ignition was reoxidized to $BaSO_4$. Calculate the true per cent S in the original sample. Calculate the per cent S which was present as sulphide and the per cent S present as sulphate, in the first ignition product.

702. In determining sulphur in steel the sulphur is eventually obtained as H_2S, an excess I_2 is added, and the excess is titrated with $Na_2S_2O_3$ solution. What weight of sample should be taken such that the cubic centimeters of $Na_2S_2O_3$ used multiplied by a factor, and subtracted from the cubic centimeters of I_2 used, will be exactly 12 times the per cent S? One cubic centimeter of the $Na_2S_2O_3$ is equivalent to the iodine liberated when 1 c.c. of K_2Cr_2O, (1 c.c. $\approx$ 0.004900 gram Fe) is treated with KI in acid solution. What is the "factor" referred to above when 1 c.c. of iodine is equivalent to 0.004900 gram of As_2O_3?

703. In the determination of sulphur by the evolution method, a notebook contains the following data:

Weight of sample = 5.0275 grams.
Iodine used = 15.59 c.c.
$Na_2S_2O_3$ used = 12.68 c.c.
1 c.c. iodine $\approx$ 1.086 c.c. $Na_2S_2O_3$.
1 c.c. $Na_2S_2O_3$ $\approx$ 0.005044 gram Cu.

Find the percentage of sulphur.

704. A 2-gram sample of steel is analyzed for chromium. A certain volume of 0.1500 N $FeSO_4$ solution is added, and the excess is titrated with 0.1000 N $KMnO_4$, requiring 30.00 c.c. If the sample contained 0.50 per cent Cr, what volume of $FeSO_4$ was added?

705. A sample of steel contains approximately 0.075 per cent sulphur. Using a 5-gram sample and determining the per cent S in an analysis involving the following equations, calculate the strength of iodine to be used so that an error of 0.20 c.c. in the titration shall represent an actual error of only 0.001 per cent in the reported percentage of sulphur.

$$MnS + 2HCl \rightarrow MnCl_2 + H_2S$$
$$CdCl_2 + H_2S + 2NH_4OH \rightarrow CdS + 2H_2O + 2NH_4Cl$$
$$CdS + 2HCl \rightarrow H_2S + CdCl_2$$
$$H_2S + I_2 \rightarrow 2HI + S.$$

706. In the evolution method for sulphur, what weight of steel will it be necessary to take for analysis so that the number of cubic centimeters of N/20 iodine solution may represent the percentage of sulphur?

707. If nitrogen is reduced to the quadrivalent state, compute the volume of fuming nitric acid actually required to oxidize 5.000 grams of pyritic ore containing 70.1 per cent FeS_2. Neglect the quantity of acid required for the remainder of the ore. Assume the acid to be of 1.500 specific gravity and to contain 94.1 per cent HNO_3 by weight. Compute the weight of dry sodium peroxide required to carry out the same oxidation, if the peroxide contains 40 per cent of sodium carbonate.

708. What weight of ferric alum should be taken for analysis such that the weight in centigrams of $BaSO_4$ obtained is equal to one-half the per cent S in the sample?

709. In the determination of sulphur in pyrite what weight of sample should be taken for analysis so that the weight of the ignited $BaSO_4$ precipitate multiplied by 25 gives the percentage of sulphur in the sample?

710. In the analysis of 0.8000 gram of a substance for sulphur by the barium chromate method, 25.00 c.c. of N/9 sodium thiosulphate solution were used. Compute the per cent sulphur.

711. The H_2S in a sample of illuminating gas is determined by passing 10 cubic feet of the gas through an absorbing agent and oxidizing the sulphur to sulphate. By the Hinman method there are used 12.00 c.c. of thiosulphate solution having two-thirds the normality as a reducing agent as a certain potassium tetroxalate solution. Six cubic centimeters of the tetroxalate will reduce in acid solution 3.00 c.c. of a $KMnO_4$ solution containing 0.00632 gram of $KMnO_4$ per cubic centimeter. What is the H_2S content of the gas in parts per thousand (by volume)?

712. What weight in grams of impure ferrous ammonium sulphate should be taken for analysis so that the number of centigrams of $BaSO_4$ obtained will represent five times the percentage of sulphur in the sample?

713. What volume of 15 N HNO_3 would be used in dissolving the Cu_2S precipitate from a 5-gram sample of steel containing 0.25 per cent Cu, if the precipitate were contaminated with 5 per cent of its weight of FeS (assume sulphur completely oxidized and the HNO_3 reduced to NO_2)?

714. What volume of water vapor at 110°C. and 28 inches of mercury pressure can be obtained by strong ignition of a 0.001-gram molecular weight of $H_2NaAl_3Si_3O_{12}.2H_2O$?

Carbon. Silicon. Titanium. Tungsten

715. What volume of 6 N hydrofluoric acid is theoretically required to volatilize the silica from 0.5000 gram of $KAlSi_3O_8$? What volume of SiF_4 at 29°C. and 765 mm. pressure is produced?

716. A sample of titanium ore is treated in such a way that all the iron is present in the bivalent condition and all the titanium in the trivalent condition. The solution is then titrated with ferric alum solution of which 50 c.c. yield 0.4000 gram of Fe_2O_3. If the original sample weighed 0.6000

gram and 15.00 c.c. of ferric alum solution were used, find the per cent TiO_2 in the ore.

717. Write the reaction for dissolving 0.06 gram of Fe_2Si in 6 N HNO_3. How much 6 N HF would be theoretically required for the silica?

718. A 3-gram sample of steel contains 3 per cent Fe_2Si. After dissolving in HNO_3 and evaporating, what weight of SiO_2 will be obtained? What volume of SiF_4 under standard conditions will be evolved?

719. A volume of 10.05 c.c. of SiF_4 at 740 mm. pressure and 21°C. corresponds to how many grams of Fe_2Si?

720. A 3-gram sample of steel containing 1.2 per cent Si and 0.2 per cent W is dissolved in concentrated HNO_3 and evaporated to dryness. What should be the weight of the ignited acid-insoluble residue before and after treatment with HF?

721. Write all equations for two methods of getting a sample of ferrotungsten into solution Calculate the weight of tungsten equivalent to 0.0102 gram of ignited tungstic acid.

722. A sample of tungsten steel weighing 5.000 grams is dissolved in aqua regia, evaporated to dryness, and dehydrated. The acid-insoluble residue weighs 0.0928 gram and after treatment with HF weighs 20 per cent less. What are the percentages of Si and of W in the steel?

723. If a 1.3-gram sample of iron containing 1.15 per cent carbon is analyzed by direct combustion, what will be the gain in weight of the ascarite tube? If the Cain method is used and the gas is passed through 100 c.c. of N/12 $Ba(OH)_2$ how many cubic centimeters of 0.1 N HCl would be required to titrate the filtrate?

724. The iron in a solution of a 0.800-gram sample of titanium ore was reduced with stannous chloride and then reacted with 26.0 c.c. of $KMnO_4$ (1 c.c. = 0.800 c.c. of potassium tetroxalate solution which is 0.0800 N as an acid). The sulphuric acid solution of a similar sample was reduced with zinc and the reduced solution was caught in an acid solution of ferric alum which then reacted with 48.0 c.c. of the above $KMnO_4$. Compute the analysis on the basis that the original sample contained only Fe_3O_4, TiO_2, and SiO_2.

725. What weight of sample should be taken such that the number of cubic centimeters of ferric solution containing 10 grams of Fe per liter required to react with the tervalent Ti in the sample shall be in the ratio to the per cent Ti in the ore as 12:3?

726. What is the percentage of carbon in a 5-gram sample of steel if on combustion the ascarite tube gains 0.1601 gram in weight? Using the same weight of sample and passing the gas into $Ba(OH)_2$ solution what must be the normality of an HCl solution so that each cubic centimeter required to titrate the $BaCO_3$ precipitate will be 25 times the per cent C?

727. A sample of steel weighing 4 grams is to be analyzed for carbon by passing the gaseous combustion products through 50 c.c. of standard $Ba(OH_2)$ solution, filtering, and titrating the filtrate with standard HCl solution. It is desired to prepare the two solutions of such normality that

by subtracting the burette reading from 100 the resulting value will be 30 times the per cent C. What must be the two normalities?

728. A solution of ferric chloride is prepared by dissolving 10.03 grams of pure iron in HCl, oxidizing, and diluting to 1 liter. If 50 c.c. of this solution react with 40 c.c. of a $TiCl_3$ solution what is the normality of the latter as a reducing agent?

Manganese. Chromium

729. What weight of pyrolusite containing 75 per cent MnO_2 will oxidize the same amount of oxalic acid as 35 c.c. of a $KMnO_4$ solution of which 1 c.c. will liberate 0.0175 gram of iodine from an excess of potassium iodide?

730. An oxide of Mn weighing 0.4580 gram is treated with dilute H_2SO_4 and 50 c.c. of tenth 0.1 N ferrous ammonium sulphate solution. After the reduction of the manganese to the manganous condition is complete, the excess of ferrous solution reacts with 30 c.c. of 0.03333 N $KMnO_4$. Find the symbol of the original oxide of Mn.

731. Given the following data in the analysis of pyrolusite by the iodimetric process, find the volume of disodium phosphate solution (90 grams of $Na_2HPO_4.12H_2O$ per liter) which would be necessary to precipitate the Mn as $MnNH_4PO_4$ from 0.5000 gram of the sample.

Weight of sample = 1 gram.
$Na_2S_2O_3$ solution = 40.4 c.c.

The thiosulphate solution is equivalent in reducing power to a stannous chloride solution which contains 29.75 grams of tin per liter.

732. What volume of bromine water (30 grams Br_2 per liter) would theoretically be required to precipitate the manganese from an acetic acid solution of its salt, if the resulting precipitate of MnO_2 gives on ignition 0.1060 gram of Mn_3O_4? ($Mn(C_2H_3O_2)_2 + Br_2 + 2H_2O \rightarrow MnO_2 + 2HBr + 2HC_2H_3O_2$.) How many cubic centimeters of sulphurous acid (specific gravity 1.028 containing 5.00 per cent SO_2 by weight) would be required to dissolve the MnO_2 precipitate ($MnO_2 + H_2SO_3 \rightarrow MnSO_4 + H_2O$) and what weight of $Mn_2P_2O_7$ would be obtained from the resulting solution?

733. A sample of pyrolusite weighs 0.2400 gram and is 92.50 per cent pure MnO_2. The iodine liberated from KI by the manganese dioxide is sufficient to react with 46.25 c.c. of $Na_2S_2O_3$ solution. What is the normality of the thiosulphate solution?

734. From the following data compute the normality of a potassium permanganate solution, and show its value in terms of manganese by the Volhard, Williams, and Bismuthate processes:

20 c.c. $KMnO_4 \simeq$ 45 c.c. $Na_2S_2O_3$.
20 c.c. $Na_2S_2O_3 \simeq$ 15 c.c. iodine.
1 c.c. iodine $\simeq$ 0.00056 gram sulphur.

735. A sample of ferro-manganese contains 80.25 per cent Mn. How many cubic centimeters of $KMnO_4$ (1 c.c. $\simeq$ 0.00500 gram Fe) were used for

the titration of a sample weighing 0.300 gram by the Volhard method? What would have been the apparent percentage if a minus error of 0.35 c.c. had been made in the burette reading of the permanganate solution?

736. From the following data compute the per cent Cr in a sample of steel. Weight of sample = 1.850 grams. After oxidation with $KMnO_4$ and removal of the excess reagent, 150 c.c. of 0.0800 N ferrous solution are added and the solution then reacts with 14.00 c.c. of 0.0900 N $KMnO_4$.

737. Find the value of 1 c.c. of 0.0833 N $KMnO_4$ in terms of Mn by the (*a*) Volhard method, (*b*) Bismuthate method, and (*c*) Williams method.

738. A sample of steel weighing 1.880 grams contains 0.596 per cent manganese, and 9.49 c.c. of permanganate solution (1 c.c. $\simeq$ 0.007188 gram sodium oxalate) are equivalent to the manganese. What method was used for the determination (Volhard? Bismuthate? Williams?)?

739. If a sample of steel weighing 0.900 gram and containing 0.50 per cent Mn is used for analysis, how many cubic centimeters of a solution of $KMnO_4$ (10 c.c. $\simeq$ 0.06300 gram of $KHC_2O_4.H_2C_2O_4.2H_2O$) will be equivalent to manganese by (*a*) the Bismuthate method, (*b*) the Volhard method, and (*c*) the Williams method?

740. In the Volhard method for manganese, what weight of steel should be taken so that the cubic centimeters of 0.1 N $KMnO_4$ shall equal ten times the per cent Mn?

741. If 50 c.c. of N/12 $KMnO_4$ solution were reduced to the manganous condition, how many cubic centimeters of N/12 $KMnO_4$ would be equivalent to the Mn in the reduced solution by the (*a*) Volhard method, (*b*) Bismuthate method, and (*c*) Williams method?

742. What weight of steel should be taken for analysis such that the cubic centimeters of N/12 $KMnO_4$ equivalent to the Mn in the steel is 8 times the per cent Mn in the steel if the analysis is made by the (*a*) Volhard method (one-half the solution is titrated), (*b*) Bismuthate method, and (*c*) Williams method?

743. Given 0.0800 N $KMnO_4$ and 0.0900 N ferrous solution, what weight of steel should be taken for analysis by the Barba method such that the cubic centimeters of $KMnO_4$ equivalent to the ferrous solution used minus the cubic centimeters of $KMnO_4$ used gives 5 times the per cent Cr?

744. A sample of chromite weighing 1.013 grams, after systematic removal of interfering substances, yields a precipitate of $PbCrO_4$ weighing 1.0423 grams. Calculate the percentage of Cr_2O_3 in the sample.

745. It is desired to prepare a solution of chromium acetate to contain 8.00 per cent Cr_2O_3 by weight for use as a mordant. A batch of the material is made up to the approximate concentration and is found to have a specific gravity of 1.195. A 2-c.c. sample is taken and the chromium is oxidized to dichromate. To one-half the solution are added 50 c.c. of ferrous sulphate solution and the excess ferrous iron requires exactly 17.32 c.c. of 0.1334 N $KMnO_4$ for oxidation (25 c.c. $FeSO_4$ solution $\simeq$ 21.73 c.c. $KMnO_4$ solution). How many pounds of water must be evaporated from one ton of the liquor to give the desired concentration?

746. What weight of pyrolusite should be taken and what should be the normality of the permanganate used to the excess of oxalic acid added to reduce the MnO_2 so that (100 × weight $H_2C_2O_4.2H_2O$ − c.c. $KMnO_4$) = per cent Mn?

747. A steel containing 0.90 per cent Cr weighs 2 grams. The chromium is oxidized to chromate and to the acidified solution is added an excess of KI. The liberated iodine requires 10.00 c.c. of thiosulphate solution. What is the normality of the thiosulphate solution?

748. In the Barba Method for chromium in steel what must be the normality of the $KMnO_4$ and of the $FeSO_4$ solution so that with a sample weighing 1.20 grams, per cent $Cr = \frac{\text{c.c. } KMnO_4 - (\text{c.c. } FeSO_4 \times 2.6)}{5}$.

General and Miscellaneous Analyses

749. From the following relationships, compute the normal concentration of each reagent and the weight of silver alloy containing 90 per cent silver which will react with 50 c.c. of the potassium thiocyanate solution:

Thirty cubic centimeters HCl ≃ 0.7950 gram of pure sodium carbonate (methyl orange as indicator).

Thirty cubic centimeters HCl react with the same quantity of sodium hydroxide solution that reacts with 40 c.c. of potassium tetroxalate solution.

Twenty cubic centimeters of the tetroxalate solution react with 90 c.c. of $KMnO_4$ solution.

Twenty-seven cubic centimeters of $KMnO_4$ solution react with an excess of KI and furnish enough iodine to react with 36 c.c. of $Na_2S_2O_3$ solution.

In terms of a normal solution the thiocyanate is found to be half as strong as the thiosulphate solution.

750. If 1.765 grams of pure $K_4Fe(CN)_6.3H_2O$ are dissolved in water and diluted to 500 c.c., calculate the normality of the solution with reference to K and to CN as precipitating agents. Calculate the normality of the solution as a reducing agent.

751. Given the following data:

35.27 c.c. I_2 solution ≃ 0.02991 gram As_2O_3.

30.00 c.c. I_2 solution ≃ 45.03 c.c. $Na_2S_2O_3$ solution.

25.82 c.c. $Na_2S_2O_3$ will reduce the iodine liberated from an excess of KI by 31.05 c.c. $KMnO_4$ solution.

15.42 c.c. $KMnO_4$ ≃ 16.97 c.c. $KHC_2O_4.H_2C_2O_4.2H_2O$ solution.

1 c.c. $KHC_2O_4.H_2C_2O_4.2H_2O$ solution ≃ 1.074 c.c. NaOH solution.

10 c.c. NaOH solution ≃ 12 c.c. HCl solution.

How many grams of $CaCO_3$ will be reacted upon by 29.83 c.c. of this HCl solution?

752. What is the relation of each of the following solutions to the normal solution?

(*a*) $Na_2S_2O_3$: 1 c.c. ≃ 0.002924 gram KIO_3.

(*b*) $KMnO_4$ (in presence of acid): 1 c.c. ≃ 0.009292 gram KHC_2O_4.

(*c*) $KMnO_4$ (same solution as above used in alkaline or neutral solution).

(*d*) As_2O_3 (as an acid): 1 c.c. $\simeq$ 0.01924 gram Na_2CO_3.

(*e*) As_2O_3 (as a reducing agent): 1 c.c. $\simeq$ 0.002492 gram $K_2Cr_2O_7$.

(*f*) As_2O_3 (as reducing agent): 1 c.c. contains 0.001426 gram As_2O_3.

(*g*) As_2O_3 (as a reducing agent): 1 c.c. $\simeq$ 0.002422 gram $KHC_2O_4.H_2C_2O_4.2H_2O$.

753. On the assumption that $Mo_{24}O_{37}$ is a mixture of MoO_3 and Mo_2O_3 what per cent of the total Mo is in the trivalent state and what per cent is in the quadrivalent state?

754. If 500 c.c. of a solution which is 0.3 N in HNO_3 and also contains 0.500 gram of Na_2MoO_4 is treated with H_2S and all the molybdenum is precipitated as MoS_3, what is the normality of the filtrate as an acid assuming that its volume is now 600 c.c.?

755. What weight of molybdenum steel should be taken so that 1 c.c. of 0.06 N $KMnO_4$ will be used for each 0.5 per cent of Mo assuming reduction of element to the trivalent condition and reoxidation by the permanganate to the valence of six?

756. A sample of limestone rock was analyzed, and the percentages of the constituents, expressed as SiO_2, Fe_2O_3, Al_2O_3, CaO, MgO, CO_2, and H_2O were obtained as follows:

SiO_2—A sample weighing 2.5000 grams was dissolved in HCl, evaporated to dryness, and dried at 110°C. The ignited insoluble residue weighed 0.6650 gram.

$Fe_2O_3 + Al_2O_3$—The filtrate from the SiO_2 determination gave a precipitate with ammonia weighing 0.2181 gram after ignition.

CaO—One-fifth of the filtrate from the above determination gave a precipitate of calcium oxalate requiring 38.40 c.c. of 0.1225 N $KMnO_4$ for oxidation.

MgO—From the filtrate of the Ca determination was obtained 0.1133 gram of $Mg_2P_2O_7$.

Fe_2O_3—A sample weighing 2.000 grams required 12.24 c.c. of the above $KMnO_4$ to oxidize all the iron after reduction.

$CO_2 + H_2O$—A sample weighing 0.5134 gram after strong ignition weighed 0.3557 gram.

CO_2—The same weight of sample on treatment with acid caused a potash bulb to gain 0.1541 gram in weight.

(*a*) What was the complete analysis as reported? (*b*) If in the analysis, the analyst overlooked the presence of 1.50 per cent of pyrite (FeS_2 is insoluble in dilute HCl and on ignition is converted into Fe_2O_3) in the rock, what was the correct percentage of Fe_2O_3, of Al_2O_3, of SiO_2, and of H_2O?

APPENDIX

Table I.—Conversion Factors

1 inch = 2.5400 centimeters.
1 centimeter = 0.39370 inch.

1 square inch = 6.4515 square centimeters.
1 square centimeter = 0.15500 square inch.

1 cubic inch = 16.387 cubic centimeters.
1 cubic centimeter = 0.061026 cubic inch.

1 quart (liquid) = 0.94636 liter.
1 liter = 1.0567 quarts (liquid).

1 pound (avoir.) = 0.45359 kilogram.
1 kilogram = 2.2046 pounds (avoir.).

1 ounce (avoir.) = 28.350 grams.
1 gram = 0.035273 ounce (avoir.).

1 grain = 0.64799 gram.
1 gram = 15.432 grains.

Degrees Centigrade = (Degrees Fahrenheit − 32) ÷ 1.8.

Degrees Fahrenheit = (Degrees Centigrade × 1.8) + 32.

Degrees Absolute = Degrees Centigrade + 273.

Table II.—Specific Gravities of Common Substances

(From various sources)

Aluminum	2.70	Mercury	13.6
Brass	8.4	Nickel	8.7
Brass (balance weights)	8.0	Platinum	21.4
Cast iron	7.3	Porcelain	2.4
Copper	8.94	Quartz	2.66
Glass (white)	2.6	Rock salt	2.15
Gold	19.3	Silver	10.5
Ivory	1.9	Steel	7.8
Lead	11.3	Sulphur	2.05
Marble	2.7	Zinc	7.10

TABLE III.—DENSITY OF DRY AIR

(From Chemiker-Kalender published by Julius Springer)

The table shows the density of dry air at temperature t and barometric pressure b.

t	b = 720 mm.	730 mm.	740 mm.	750 mm.	760 mm.	770 mm.
0°	0.001225	0.001242	0.001259	0.001276	0.001293	0.001310
1	1221	1238	1255	1272	1289	1306
2	1216	1233	1250	1267	1284	1301
3	1212	1229	1246	1262	1279	1296
4	1208	1224	1241	1258	1275	1291
5	1203	1220	1237	1253	1270	1287
6	1199	1216	1232	1249	1266	1282
7	1195	1211	1228	1244	1261	1278
8	1190	1207	1223	1240	1257	1273
9	1186	1203	1219	1236	1252	1269
10°	1182	1198	1215	1231	1248	1264
11	1178	1194	1211	1227	1243	1260
12	1174	1190	1206	1223	1239	1255
13	1170	1186	1202	1218	1235	1251
14	1165	1182	1198	1214	1230	1246
15	1161	1178	1194	1210	1226	1242
16	1157	1174	1190	1206	1222	1238
17	1153	1169	1185	1201	1218	1234
18	1149	1165	1181	1197	1213	1229
19	1146	1161	1177	1193	1209	1225
20°	1142	1157	1173	1189	1205	1221
21	1138	1154	1169	1185	1201	1217
22	1134	1150	1165	1181	1197	1213
23	1130	1146	1161	1177	1193	1209
24	1126	1142	1158	1173	1189	1204
25	1122	1138	1154	1169	1185	1200
26	1119	1134	1150	1165	1181	1196
27	1115	1130	1146	1161	1177	1192
28	1111	1127	1142	1158	1173	1188
29	1108	1123	1138	1154	1169	1184
30°	1104	1119	1135	1150	1165	1181

Table IV.—Vapor Pressure of Water

(Regnault)

(From Treadwell and Hall's "Analytical Chemistry," Vol. II, published by John Wiley & Sons, Inc., by permission)

In Millimeters

Temp., °C.	.0	.1	.2	.3	.4	.5	.6	.7	.8	.9
0	4.60	4.63	4.67	4.70	4.73	4.77	4.80	4.84	4.87	4.91
1	4.94	4.98	5.01	5.05	5.08	5.12	5.16	5.19	5.23	5.27
2	5.30	5.34	5.38	5.42	5.45	5.49	5.53	5.57	5.61	5.65
3	5.69	5.73	5.77	5.81	5.85	5.89	5.93	5.97	6.01	6.06
4	6.10	6.14	6.18	6.23	6.27	6.31	6.36	6.40	6.45	6.49
5	6.53	6.58	6.63	6.67	6.72	6.76	6.81	6.86	6.90	6.95
6	7.00	7.05	7.10	7.14	7.19	7.24	7.29	7.34	7.39	7.44
7	7.49	7.54	7.60	7.65	7.70	7.75	7.80	7.86	7.91	7.96
8	8.02	8.07	8.13	8.18	8.24	8.29	8.35	8.40	8.46	8.52
9	8.57	8.63	8.69	8.75	8.81	8.87	8.93	8.99	9.05	9.11
10	9.17	9.23	9.29	9.35	9.41	9.47	9.54	9.60	9.67	9.73
11	9.79	9.86	9.92	9.99	10.05	10.12	10.19	10.26	10.32	10.39
12	10.46	10.53	10.60	10.67	10.73	10.80	10.88	10.95	11.02	11.09
13	11.16	11.24	11.31	11.38	11.46	11.53	11.61	11.68	11.76	11.83
14	11.91	11.99	12.06	12.14	12.22	12.30	12.38	12.46	12.54	12.62
15	12.70	12.78	12.86	12.95	13.03	13.11	13.20	13.28	13.37	13.45
16	13.54	13.62	13.71	13.80	13.89	13.97	14.06	14.15	14.24	14.33
17	14.42	14.51	14.61	14.70	14.79	14.88	14.98	15.07	15.17	15.26
18	15.36	15.45	15.55	15.65	15.75	15.85	15.95	16.05	16.15	16.25
19	16.35	16.45	16.55	16.66	16.76	16.86	16.97	17.07	17.18	17.29
20	17.39	17.50	17.61	17.72	17.83	17.94	18.05	18.16	18.27	18.38
21	18.50	18.61	18.72	18.84	18.95	19.07	19.19	19.31	19.42	19.54
22	19.66	19.78	19.90	20.02	20.14	20.27	20.39	20.51	20.64	20.76
23	20.89	21.02	21.14	21.27	21.40	21.53	21.66	21.79	21.92	22.05
24	22.18	22.32	22.45	22.59	22.72	22.86	23.00	23.14	23.27	23.41
25	23.55	23.69	23.83	23.98	24.12	24.26	24.41	24.55	24.70	24.84
26	24.99	25.14	25.29	25.44	25.59	25.74	25.89	26.05	26.20	26.35
27	26.51	26.66	26.82	26.98	27.14	27.29	27.46	27.62	27.78	27.94
28	28.10	28.27	28.43	28.60	28.77	28.93	29.10	29.27	29.44	29.61
29	29.78	29.96	30.13	30.31	30.48	30.65	30.83	31.01	31.19	31.37
30	31.55	31.73	31.91	32.09	32.28	32.46	32.65	32.84	33.03	33.22
31	33.41	33.60	33.79	33.98	34.17	34.37	34.56	34.76	34.96	35.16
32	35.36	35.56	35.76	35.96	36.17	36.37	36.58	36.78	36.99	37.20
33	37.41	37.62	37.83	38.05	38.26	38.47	38.69	38.91	39.12	39.34
34	39 57	39.79	40.01	40.23	40.46	40.68	40.91	41.14	41.36	41.60

Table V.—Relative Density of Water

(From the "Handbook of Chemistry and Physics," published by the Chemical Rubber Co., Cleveland, Ohio, by permission)

The mass of one cubic centimeter of water at 4°C. is taken as unity.

The absolute density in C. G. S. units is obtained by multiplying the relative density by 0.999973.

(Smithsonian Tables, compiled from Various Authors)

Temp., °C.	Density	Temp., °C.	Density	Temp., °C.	Density
+0	0.99987	22	780	43	107
1	993	23	756	44	066
2	997	24	732	45	0 99025
3	999	25	0.99707	46	0.98982
4	1.00000	26	681	47	940
5	0.99999	27	654	48	896
6	997	28	626	49	852
7	993	29	597	50	0.98807
8	988	30	0.99567	51	762
9	981	31	537	52	715
10	0.99973	32	505	53	669
11	963	33	473	54	621
12	952	34	440	55	0 98573
13	940	35	0.99406	60	324
14	927	36	371	65	059
15	0.99913	37	336	70	0.97781
16	897	38	299	75	489
17	880	39	262	80	0.97183
18	862	40	0.99224	85	0.96865
19	843	41	186	90	534
20	0.99823	42	147	95	192
21	802				

Table VI.—Sensitiveness of Indicators

(From various sources)

The table gives the approximate hydrogen-ion and hydroxide-ion concentrations required to produce the indicated change of color in dilute solutions (0.001 per cent) of the more common indicators.

Concentration of H^+..	1×10^{-9}	1×10^{-8}	1×10^{-7}	1×10^{-6}	1×10^{-5}	1×10^{-4}	1×10^{-3}
Concentration of OH^-	1×10^{-5}	1×10^{-6}	1×10^{-7}	1×10^{-8}	1×10^{-9}	1×10^{-10}	1×10^{-11}
Phenolphthalein.....	Pink	Colorless					
Litmus.....		Violet-blue	Violet	Violet-pink			
Methyl red.....				Yellow	Pink		
Methyl orange.....					Yellow	Orange	Pink
Congo red.....					Red	Violet	Blue

Table VII.—Effect of Indicator on the Titration of Common Acids

(R. T. Thomson)

(From Cohn's "Indicators and Test Papers," John Wiley & Sons, publishers, by permission)

The table shows the number of hydrogen atoms replaced by NaOH or KOH when a compound approximately neutral to the indicator is formed. The blank spaces indicate that the end-reaction is obscure.

Acid	Formula	Methyl-orange cold	Phenolphthalein		Litmus	
			Cold	Boiling	Cold	Boiling
Sulphuric.....	H_2SO_4	2	2	2	2	2
Hydrochloric.....	HCl	1	1	1	1	1
Nitric.....	HNO_3	1	1	1	1	1
Thiosulphuric.....	$H_2S_2O_3$	2	2	2	2	2
Carbonic.....	H_2CO_3	0	1 dilute	0	..	0
Sulphurous.....	H_2SO_3	1	2	..	..	..
Hydrosulphuric.....	H_2S	0	1 dilute	0	..	0
Phosphoric.....	H_3PO_4	1	2	..	..	..
Arsenic.....	H_3AsO_4	1	2	..	..	..
Arsenous.....	H_3AsO_3	0	..	..	0	0
Nitrous.....	HNO_2	indicator destroyed	1	..	1	..
			..	..	..	..
Silicic.....	H_4SiO_4	0	..	..	0	0
Boric.....	H_3BO_3	0	..	..	..	..
Chromic.....	H_2CrO_4	1	2	2	..	..
Oxalic.....	$H_2C_2O_4$	..	2	2	2	2
Acetic.....	$HC_2H_3O_2$	..	1	..	1 nearly	..
Butyric.....	$HC_4H_7O_2$	..	1	..	1 nearly	..
Succinic.....	$H_2C_4H_4O_4$	..	2	..	2 nearly	..
Lactic.....	$HC_3H_5O_3$	..	1	..	1	..
Tartaric.....	$H_2C_4H_4O_6$	..	2	..	2	..
Citric.....	$H_3C_6H_5O_7$	..	3	..	..	..

TABLE VIII.—ESSENTIAL COMPOSITION OF A FEW COMMON MINERALS

Apatite	$Ca_3(PO_4)_2.Ca(F, Cl)_2$
Barite	$BaSO_4$
Bauxite	Al_2O_3
Calcite	$CaCO_3$
Cassiterite	SnO_2
Chromite (chrome iron ore)	$FeCr_2O_4$
Cinnabar	HgS
Corundum	Al_2O_3
Cryolite	$3NaF.AlF_3$
Dolomite	$CaMg(CO_3)_2$
Feldspar	$KAlSi_3O_8$
Fluorite	CaF_2
Galena	PbS
Gypsum	$CaSO_4.2H_2O$
Limestone	$(Ca, Mg)CO_3$
Limonite	Fe_2O_3
Magnetite	Fe_3O_4
Pyrolusite	MnO_2
Pyrite	FeS_2
Quartz	SiO_2
Rutile	TiO_2
Siderite	$FeCO_3$
Spathic iron ore	$FeCO_3$
Sphalerite	ZnS
Stibnite	Sb_2S_3

TABLE IX.—SPECIFIC GRAVITY OF STRONG ACIDS AT $\frac{15^\circ}{4^\circ}$ IN VACUO

(According to G. Lunge)

(From Treadwell and Hall's "Analytical Chemistry," Vol. II, published by John Wiley & Sons, Inc., by permission)

Specific gravity at $\frac{15^\circ}{4^\circ}$ (vacuo)	Per cent by weight			Specific gravity at $\frac{15^\circ}{4^\circ}$ (vacuo)	Per cent by weight	
	HCl	HNO_3	H_2SO_4		HNO_3	H_2SO_4
1.000	0.16	0.10	0.09	1.235	37.53	31.70
1.005	1.15	1.00	0.95	1.240	38.29	32.28
1.010	2.14	1.90	1.57	1.245	39.05	32.86
1.015	3.12	2.80	2.30	1.250	39.82	33.43
1.020	4.13	3.70	3.03	1.255	40.58	34.00
1.025	5.15	4.60	3.76	1.260	41.34	34.57
1.030	6.15	5.50	4.49	1.265	42.10	35.14
1.035	7.15	6.38	5.23	1.270	42.87	35.71
1.040	8.16	7.26	5.96	1.275	43.64	36.29
1.045	9.16	8.13	6.67	1.280	44.41	36.87
1.050	10.17	8.99	7.37	1.285	45.18	37.45
1.055	11.18	9.84	8.07	1.290	45.95	38.03
1.060	12.19	10.68	8.77	1.295	46.72	38.61
1.065	13.19	11.51	9.47	1.300	47.49	39.19
1.070	14.17	12.33	10.19	1.305	48.26	39.77
1.075	15.16	13.15	10.90	1.310	49.07	40.35
1.080	16.15	13.95	11.60	1.315	49.89	40.93
1.085	17.13	14.74	12.30	1.320	50.71	41.50
1.090	18.11	15.53	12.99	1.325	51.53	42.08
1.095	19.06	16.32	13.67	1.330	52.37	42.66
1.100	20.01	17.11	14.35	1.335	53.22	43.20
1.105	20.97	17.89	15.03	1.340	54.07	43.74
1.110	21.92	18.67	15.71	1.345	54.93	44.28
1.115	22.86	19.45	16.36	1.350	55.79	44.82
1.120	23.82	20.23	17.01	1.355	56.66	45.35
1.125	24.78	21.00	17.66	1.360	57.57	45.88
1.130	25.75	21.77	18.31	1.365	58.48	46.41
1.135	26.70	22.54	18.96	1.370	59.39	46.94
1.140	27.66	23.31	19.61	1.375	60.30	47.47
1.145	28.61	24.08	20.26	1.380	61.27	48.00
1.150	29.57	24.84	20.91	1.385	62.24	48.53
1.155	30.55	25.60	21.55	1.390	63.23	49.06
1.160	31.52	26.36	22.19	1.395	64.25	49.59
1.165	32.49	27.12	22.83	1.400	65.30	50.11
1.170	33.46	27.88	23.47	1.405	66.40	50.63
1.175	34.42	28.63	24.12	1.410	67.50	51.15
1.180	35.39	29.38	24.76	1.415	68.63	51.66
1.185	36.31	30.13	25.40	1.420	69.80	52.15
1.190	37.23	30.88	26.04	1.425	70.98	52.63
1.195	38.16	31.62	26.68	1.430	72.17	53.11
1.200	39.11	32.36	27.32	1.435	73.39	53.59
1.205	.....	33.09	27.95	1.440	74.68	54.07
1.210	.....	33.82	28.58	1.445	75.98	54.55
1.215	.....	34.55	29.21	1.450	77.28	55.03
1 220	.....	35.28	29.84	1.455	78.60	55.50
1.225	.....	36.03	30.48	1.460	79.98	55.97
1.230	.....	36.78	31.11	1.465	81.42	56.43

SPECIFIC GRAVITY OF STRONG ACIDS AT $\frac{15^\circ}{4^\circ}$ IN VACUO.—(*Continued*)

(According to G. Lunge)

Specific gravity at $\frac{15^\circ}{4^\circ}$ (vacuo)	Per cent by weight		Specific gravity at $\frac{15^\circ}{4^\circ}$ (vacuo)	Per cent by weight	Specific gravity at $\frac{15^\circ}{4^\circ}$ (vacuo)	Per cent by weight
	HNO_3	H_2SO_4		H_2SO_4		H_2SO_4
1.470	82.90	56.90	1.610	69.56	1.750	81.56
1.475	84.45	57.37	1.615	70.00	1.755	82.00
1.480	86.05	57.83	1.620	70.42	1.760	82.44
1.485	87.70	58.28	1.625	70.85	1.765	83.01
1.490	89.90	58.74	1.630	71.27	1.770	83.51
1.495	91.60	59.22	1.635	71.70	1.775	84.02
1.500	94.09	59.70	1.640	72.12	1.780	84.50
1.505	96.39	60.18	1.645	72.55	1.785	85.10
1.510	98.10	60.65	1.650	72.96	1.790	85.70
1.515	99.07	61.12	1.655	73.40	1.795	86.30
1.520	99.67	61.59	1.660	73.81	1.800	86.92
1.525	.....	62.06	1.665	74.24	1.805	87.60
1.530	.....	62.53	1.670	74.66	1.810	88.30
1.535	.....	63.00	1.675	75.08	1.815	89.16
1.540	.....	63.43	1.680	75.50	1.820	90.05
1.545	.....	63.85	1.685	75.94	1.825	91.00
1.550	.....	64.26	1.690	76.38	1.830	92.10
1.555	.....	64.67	1.695	76.76	1.835	93.56
1.560	.....	65.20	1.700	77.17	1.840	95.60
1.565	.....	65.65	1.705	77.60	1.8405	95.95
1.570	.....	66.09	1.710	78.04	1.8410	96.38
1.575	.....	66.53	1.715	78.48	1.8415	97.35
1.580	.....	66.95	1.720	78.92	1.8410	98.20
1.585	.....	67.40	1.725	79.36	1.8405	98.52
1.590	.....	67.83	1.730	79.80	1.8400	98.72
1.595	.....	68.26	1.735	80.24	1.8395	98.77
1.600	.....	68.70	1.740	80.68	1.8390	99.12
1.605	.....	69.13	1.745	81.12	1.8385	99.31

TABLE X.—SPECIFIC GRAVITY OF POTASSIUM AND SODIUM HYDROXIDE SOLUTIONS AT 15°C.

(From Treadwell and Hall's "Analytical Chemistry," Vol. II, published by John Wiley & Sons Inc. by permission)

Specific gravity	Per cent KOH	Per cent NaOH	Specific gravity	Per cent KOH	Per cent NaOH
1.007	0.9	0.61	1.252	27.0	22.64
1.014	1.7	1.20	1.263	28.2	23.67
1.022	2.6	2.00	1.274	28.9	24.81
1.029	3.5	2.71	1.285	29.8	25.80
1.037	4.5	3.35	1.297	30.7	26.83
1.045	5.6	4.00	1.308	31.8	27.80
1.052	6.4	4.64	1.320	32.7	28.83
1.060	7.4	5.29	1.332	33.7	29.93
1.067	8.2	5.87	1.345	34.9	31.22
1.075	9.2	6.55	1.357	35.9	32.47
1.083	10.1	7.31	1.370	36.9	33.69
1.091	10.9	8.00	1.383	37.8	34.96
1.100	12.0	8.68	1.397	38.9	36.25
1.108	12.9	9.42	1.410	39.9	37.47
1.116	13.8	10.06	1.424	40.9	38.80
1.125	14.8	10.97	1.438	42.1	39.99
1.134	15.7	11.84	1.453	43.4	41.41
1.142	16.5	12.64	1.468	44.6	42.83
1.152	17.6	13.55	1.483	45.8	44.38
1.162	18.6	14.37	1.498	47.1	46.15
1.171	19.5	15.13	1.514	48.3	47.60
1.180	20.5	15.91	1.530	49.4	49.02
1.190	21.4	16.77	1.546	50.6	
1.200	22.4	17.67	1.563	51.9	
1.210	23.3	18.58	1.580	53.2	
1.220	24.2	19.58	1.597	54.5	
1.231	25.1	20.59	1.615	55.9	
1.241	26.1	21.42	1.634	57.5	

TABLE XI.—SPECIFIC GRAVITY OF AMMONIA SOLUTIONS AT 15°C.

(According to Lunge and Wiernik)

(From Treadwell & Hall's "Analytical Chemistry," Vol. II, published by John Wiley & Sons, Inc. by permission)

Specific gravity	Per cent NH_3	Specific gravity	Per cent NH_3
1.000	0.00	0.940	15.63
0.998	0.45	0.938	16.22
0.996	0.91	0.936	16.82
0.994	1.37	0.934	17.42
0.992	1.84	0.932	18.03
0.990	2.31	0.930	18.64
0.988	2.80	0.928	19.25
0.986	3.30	0.926	19.87
0.984	3.80	0.924	20.49
0.982	4.30	0.922	21.12
0.980	4.80	0.920	21.75
0.978	5.30	0.918	22.39
0.976	5.80	0.916	23.03
0.974	6.30	0.914	23.68
0.972	6.80	0.912	24.33
0.970	7.31	0.910	24.99
0.968	7.82	0.908	25.65
0.966	8.33	0.906	26.31
0.964	8.84	0.904	26.98
0.962	9.35	0.902	27.65
0.960	9.91	0.900	28.33
0.958	10.47	0.898	29.01
0.956	11.03	0.896	29.69
0.954	11.60	0.894	30.37
0.952	12.17	0.892	31.05
0.950	12.74	0.890	31.75
0.948	13.31	0.888	32.50
0.946	13.88	0.886	33.25
0.944	14.46	0.884	34.10
0.942	15.04	0.882	34.95

TABLE XII.—IONIZATION CONSTANTS

	Constant for 1st hydrogen	Constant for 2nd hydrogen	Constant for 3rd hydrogen
Acetic acid, $HC_2H_3O_2$	1.8×10^{-5}		
Boric acid, H_3BO_3	5×10^{-10}		
Carbonic acid, H_2CO_3	3×10^{-7}	3×10^{-11}	
Hydrocyanic acid, HCN	7×10^{-10}		
Hydrogen sulphide, H_2S	9.1×10^{-8}	1.2×10^{-15}	
Hypochlorous acid, HClO	4×10^{-8}		
Nitrous acid, HNO_2	4.5×10^{-4}		
Oxalic acid, $H_2C_2O_4$	3.8×10^{-2}	4.9×10^{-5}	
Phosphoric acid, H_3PO_4	1.1×10^{-2}	2×10^{-7}	3.6×10^{-13}
Sulphurous acid, H_2SO_3	1.7×10^{-2}	5×10^{-6}	

Ammonium hydroxide	1.8×10^{-5}
Aniline	4×10^{-10}
Methyl amine	5×10^{-4}
Silver hydroxide	1.1×10^{-4}

TABLE XIII.—INTERNATIONAL ATOMIC WEIGHTS, 1925

	Symbol	Atomic weight		Symbol	Atomic weight
Aluminum	Al	26.97	Molybdenum	Mo	96.0
Antimony	Sb	121.77	Neodymum	Nd	144.27
Argon	A	39.91	Neon	Ne	20.2
Arsenic	As	74.96	Nickel	Ni	58.69
Barium	Ba	137.37	Nitrogen	N	14.008
Bismuth	Bi	209.00	Osmium	Os	190.8
Boron	B	10.82	Oxygen	O	16.000
Bromine	Br	79.916	Palladium	Pd	106.7
Cadmium	Cd	112.41	Phosphorus	P	31.027
Caesium	Cs	132.81	Platinum	Pt	195.23
Calcium	Ca	40.07	Potassium	K	39.096
Carbon	C	12.000	Praseodymium	Pr	140.92
Cerium	Ce	140.25	Radium	Ra	225.95
Chlorine	Cl	35.457	Rhodium	Rh	102.91
Chromium	Cr	52.01	Rubidium	Rb	85.44
Cobalt	Co	58.94	Ruthenium	Ru	101.7
Columbium	Cb	93.1	Samarium	Sa	150.43
Copper	Cu	63.57	Scandium	Sc	45.10
Dysprosium	Dy	162.52	Selenium	Se	79.2
Erbium	Er	167.7	Silicon	Si	28.06
Europium	Eu	152.0	Silver	Ag	107.880
Fluorine	F	19.00	Sodium	Na	22.997
Gadolinium	Gd	157.26	Strontium	Sr	87.63
Gallium	Ga	69.72	Sulphur	S	32.064
Germanium	Ge	72.60	Tantalum	Ta	181.5
Glucinum[1]	Gl	9.02	Tellurium	Te	127.5
Gold	Au	197.2	Terbium	Tb	159.2
Helium	He	4.00	Thallium	Tl	204.39
Hydrogen	H	1.008	Thorium	Th	232.15
Indium	In	114.8	Thulium	Tm	169.4
Iodine	I	126.932	Tin	Sn	118.70
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.84	Tungsten	W	184.0
Krypton	Kr	82.9	Uranium	U	238.17
Lanthanum	La	138.90	Vanadium	V	50.96
Lead	Pb	207.20	Xenon	Xe	130.2
Lithium	Li	6.940	Ytterbium	Yb	173.6
Lutecium	Lu	175.0	Yttrium	Y	88.9
Magnesium	Mg	24.32	Zinc	Zn	65.38
Manganese	Mn	54.93	Zirconium	Zr	91.
Mercury	Hg	200.6			

[1] Also called Beryllium, Be.

TABLE XIV.—LOGARITHMS OF NUMBERS

Natural numbers	0	1	2	3	4	5	6	7	8	9	Proportional parts								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

TABLE XIV.—(*Continued*)

Natural numbers	0	1	2	3	4	5	6	7	8	9	Proportional parts								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9026	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

Table XV.—Antilogarithms

Logarithms	0	1	2	3	4	5	6	7	8	9	Proportional parts								
											1	2	3	4	5	6	7	8	9
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

TABLE XV.—(*Continued*)

Logarithms	0	1	2	3	4	5	6	7	8	9	Proportional parts								
											1	2	3	4	5	6	7	8	9
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

INDEX

A

Absorbing agents of gas analysis, 154
Absorption methods, 154
Acid mixtures, titration of, 115
Acid oxalates, equivalent weight of, 126
Acidimetry, calculations of, 80
Alkalimetry, calculations of, 80
Ampere, definition of, 51
Atomic weights, calculation of, 46
Avogadro's law, 149

B

Balance, sensitiveness of, 16
Balance weights, calibration of, 18
Bismuthate method for manganese, 132
Boyle's law, 147
Bromate, equivalent weight of, 124

C

Calibration of measuring instruments, 71
Carbonate mixtures, titration of, 107
Charles' law, 148
Chemical balance, sensitiveness of, 16
Chemical factor, application of to computations, 34
  definition of, 31
Chlorate, equivalent weight of, 124
Combining weight, definition of, 47
Combustion methods, 155
Concentration cell, 166
Concentration, means of expressing, 76
Constituent, elimination of, 59
  introduction of, 59
Coulomb, definition of, 51
Cubic centimeter, definition of, 71
Current efficiency, 54

D

Dalton's law, 149
Daniell cell, 163
Definite proportions, law of, 29
Deviation measures, 2
Dichromate, equivalent weight of, 122
Double indicators, 104
Dulong and Petit, law of, 47

E

Electrolysis, analysis by, 51
Electrometric titrations, 163
  titration apparatus, 142
Electromotive series, 163
Elimination of a constituent, 59
Empirical formulae, calculation of, 63
Equations, balancing of, 9
  calculations from, 29
Equilibrium constants, 23
Equivalent weight, applied to acidimetry, 80
  applied to oxidation and reduction, 119
  applied to precipitation, 142
  definition of, 78
  relation to indicator used, 103
Erg, definition of, 55

F

Factor weight sample, 36
Faraday, definition of, 52

Faraday's laws, 51
Fuming sulphuric acid, titration of, 116

G

Gas absorption methods, 154
Gas analysis, calculations of, 147
  divisions of, 147
  fundamental laws of, 147
Gas volumetric methods, divisions of, 149
Gay Lussac's law, 149
Gram atomic weight, definition of, 47
Gram equivalent weight, definition of, 78
Gravimetric analysis, calculations of, 29

H

Hydrogen peroxide, equivalent weight of, 127
  structural formula of, 128

I

Indicators, analyses involving two, 104
  relation to equivalent weight, 103
  sensitiveness of, 100
Indirect analyses, 43
Introduction of a constituent, 59
Iodate, equivalent weight of, 124
Iodine, equivalent weight of, 123
Ionization constant, 23
Isomorphic replacement, 65

J

Joule, definition of, 55

L

Liebig method for cyanide, 143
Liter, definition of, 71

M

Mass action, law of, 23
Mean deviation, 2
Mean value, 2
Measuring instruments, calibration of, 71
Milliequivalent weight, definition of, 78
Mixed alkali, titrations with two indicators, 112
Mixtures, determination of components of, 98
Mohr liter, calculation of, 73
  definition of, 73
Molal concentration, 77
Molal solution, definition of, 77
Mole, definition of, 77
Molecular formulae, calculation of, 63

N

Nernst formula, 165
  application of to electrometric titrations, 167
Nickel, volumetric determination of, 143
Nitric acid, equivalent weight of, 123
Normal concentration, 78
Normal solution, definition of, 78
Normal temperature, definition of, 71
Normal value, definition of, 78
Normality, adjusting to desired, 84
  definition of, 78
  determination of from preparation, 87
  determination of by titration, 89
  of mixed solutions, 86
Number, definition of, 3

O

Ohm, definition of, 55
Ohm's law, 55
Oleum, titration of, 116

Oxalates, equivalent weight of, 126
Oxalic acid, equivalent weight of, 126
  structural formula of, 126
Oxidation, definition of, 119
Oxidation potential series, 164
Oxidation and reduction, calculation of, 129
  electrometric titrations, 170
Oxidizing agents, equivalent weights of, 119

P

Pʜ value, 168
Percentage purity, calculation of from titration, 91
Permanganates, equivalent weight of, 121
Peroxides, equivalent weight of, 127
Persulphate method for manganese, 132
Polybasic acids, 25
Potassium acid oxalate, equivalent weight of, 126
Potassium dichromate, equivalent weight of, 122
Potassium permanganate, equivalent weight of, 121
Potassium tetroxalate, equivalent weight of, 126
Precipitation methods, calculations of, 142
Precision of measurements, 3

R

Reacting solutions, ratio of, 83
Reduction, definition of, 119
Reduction potential series, 164
Reliability, factors influencing, 1
Reported percentages, calculations from, 59

S

Saturation methods, calculations of, 142
Sensitiveness of indicators, 100
Significant figure, definition of, 3
  rules governing use of, 3
Sodium tetrathionate, structural formula of, 125
Sodium thiosulphate, equivalent weight of, 124
  structural formula of, 125
Solubility product, 26
Solutions, adjusting to desired normality, 84
  methods of standardizing, 87
  normality of mixed, 86
Specific heat, definition of, 47
Standard solutions, 76
Sulphur, equivalent weight of, 128

T

Thiosulphate, equivalent weight of 124
True liter, calculation of, 71
  definition of, 71

V

Vacuo, reduction to, 16
Valence changes in analytical work, 14
Vapor pressure, correction for, 150
Volhard method for manganese, 133
Volt, definition of, 55
Volume of reagent, calculation of, 39
Volume, relation to percentage, 96
Volumetric analysis, divisions of, 79

W

Water vapor, correction for, 150
Watt, definition of, 55
Weights, calibration of, 18
  conversion of, 16
Williams method for manganese, 132